Polymers for Packaging and Containers in Food Industry

> L.A. Sukhareva O.A. Legonkova V.S. Yakovlev

> > Edited by G.E. Zaikov

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Introduction

Development of the concept of long-term food storage is an independent field of scientific and applied research using polymers of various chemical compositions and structures.

It includes elaboration of technology of storing food products and food staples using advanced packaging materials. Their development is based on studies of temporal regularities of the quality of products depending on chemical composition, properties and structure. External factors are to be considered, too; they include conditions and terms of storage, air temperature and humidity, biocide properties of container/packaging materials, quality assessment criteria in turning out/accepting products and in long-time storage.

Based on the studies of the dynamics of the process, analysis of numerous results of research, it became possible to predict the regularities in the change of quality and terms of product storage, as well as the criteria of the impact of containers and packaging on them.

Food products are a complex object; various physico-chemical processes occur in them in production and storage, thus changing their properties and nutritive value. Such basic ingredients as proteins, lipids, carbohydrates are polyfunctional compounds, which are involved in diverse intra- and intercellular interactions.

Despite the diversity and complexity of food products, they are an integral biological system with its characteristic features. The basis of the organization of biologically active food systems are variability, preservation and stability.

A determining factor in the development of the scientific approach to storage of food products is the variability of the properties, and storage appears to be the unity of changes and preservation, variability and stability.

The properties of food products and their changes in storage should be considered under conditions of the multi-factor relationship of internal and external effects.

Stability of food products in storage is characterized by processes, which lead to a decrease of the consumer properties of foodstuffs. The directedness of these processes is determined by internal factors and initial properties of a product: the peculiarities of chemical composition, ratio of the main components, activity of the enzyme systems, occurrence of natural antioxidants. This system is affected by external factors capable of inhibiting or activating the active processes in food products. There is an exchange between the medium and the product – an exchange of mass, energy and information.

A system becomes stable and reliable when it is capable of reacting to the influence of an external medium by changing it in accordance with its inherent properties. Food products, which are biological systems, do not passively obey the influence of the external medium but actively counteract it, following its own processes due to its potentialities, its resistance to the effects of individual factors. Therefore, the ability of food products to react to an external effect is considered to be an essential factor of self-preservation.

2 INTRODUCTION

Of great importance in long-time storage of food products are polymers for containers and packaging. For an open system, a container is a barrier between a product and external factors. The requirements to containers are dictated by the properties of a product and the character of its mass exchange with the external medium.

In products suitable for long-time storage, biological (microbial, enzymic) processes are completely or almost completely excluded. Products with low moisture content (not higher than 10%) can be attributed to such products. Products with average (10 to 40%) and high (over 40%) moisture content are capable of retaining their properties for a rather limited period of time. Preservation (sterilization, freezing, sublimation etc.) makes it possible to considerably increase their storage time. Therefore, products suitable for long-time storage are those with low moisture content or preserved in various ways.

The basis of long-time storage of food products is the maximum preservation of consumer properties by regulating the initial-quality change as a result of product ageing, effects of external factors, choice of containers and packaging materials.

The main processes in food products in long-time storage, which govern the guarantee storage times, are as follows:

• for products with low moisture content: exchange of moisture with the external medium and the oxidative process;

• for frozen meat: heat exchange and oxidation reactions;

• for sterilized preserves: changes in the protein and lipid composition as well as interaction of the product with container's metal.

Of great importance is the development of container/packaging materials for storage and transportation of high-calorie foodstuffs under extreme conditions. They are manufactured for persons whose activity is related to prolonged physical and neuro-emotional stresses under unfavourable conditions.

The assortment of these foodstuffs comprises dairy, meat, fish, fruit-and-vegetable and other products, preserved by methods of thermal sterilization, sublimation drying, partial dehydration, including:

• dairy products – sources of readily assimilable calcium, complete protein and fat. They include milk beverages and curd products of sublimation drying, with added coffee, cocoa, nuts, sea-buckthorn oil; puree from dried apricots, cranberry etc.;

• sublimation-dried sour-milk products providing normalization of intestinal microflora, which is especially important in long-term consumption of preserved food;

• high-fat sterilized milk preserves, including cheeses, sterilized curd products, which are distinguished by a high content of readily assimilable protein, optimal calcium to phosphorus ratio, increased content of potassium, high energy value;

• fish products (preserves and products of sublimation drying): sources of complete readily assimilable protein, fats with a high content of polyunsaturated fatty acids, oil-soluble vitamins, major nutrients and trace elements;

• meat and meat-and-cereal products (preserves, lunch packs of sublimation drying): sources of complete protein with a balanced amino acid content owing to a combination of animal and plant protein, minerals, as well as fats with a sufficient amount of polyunsaturated fatty acids and oil-soluble vitamins in their composition;

• fruit-and-vegetable products (fruit concentrates, vegetable side dishes, juices, kissels and compotes of sublimation drying): sources of readily assimilable carbohydrates, mine-rals (potassium, trace elements), vitamins, pectins, organic acids;

• confectionary products distinguished by a high nutritive value at a minimum weight and volume;

• dehydrated beverages (tea, coffee) with readily assimilable carbohydrates added.

Ready-to-eat products need minimum preparation, are portioned and are convenient to use directly from the packaging container.

Lately, an important role is allotted to the biological safety of products, which is related to the consumption of food produced from genetically modified plants. Only in the recent years, the global acreage of transgenic crops, such as soy, maize, tomatoes and potatoes increased more than 20-fold. Food products from them are already supplied to the table of American and Russian consumers.

Norms and methods for the integrated assessment of the safety of genetically modified sources of food are intensively worked out at present. Much attention is also given to the development of advanced containers and packaging materials.

Principles of creating active packaging for food production have been proposed. Traditional basic qualities of food packaging are usually related to its inertness due to the intrinsic barrier properties of the polymer matrix. At present, the functions of packaging are much broader. The quality of a packaging is assessed by its involvement in the preservation of the nutritive value of a product, by its activity determined by such functions as the ability to regulate the speed and temperature of foodstuff heating in a microwave oven; to create an optimal gas medium inside the envelope; to change directionally the intranutrient composition of a product; to introduce flavouring materials, preservatives, gas absorbents, moisture adsorbents, antimicrobial preparations; as well as to use special coatings to improve the appearance and decorative properties of a packaging.

The purpose and functions of polymer and combined aseptic packaging have broaden.

The modern approach to packaging engineering of the 21 century is considered with account for three directions of the development of active packaging, which, as the result of introducing special additives, affects the quality of food products.

The first way of creating active packaging is based on the principles of forming a regulated modified gas medium using special membranes, adsorbents of oxygen, ethylene, for instance, in storage of fruits and vegetables.

The second way is to impart a biocide activity to the packaging with respect to pathogenic microflora in the process of production and storage. The third way: in production of food products (cheeses, uncooked dry-cured sausages) the packaging should regulate the biochemical transformations in the product for directed regulation of its properties. In this connection, immobilized bacterial cells and enzymes are introduced into the active packaging.

A topical problem is to develop ecologically harmless container/packaging materials and coatings due to the aggravated situation with providing healthy food in the right quantities. A decrease in the level of production, crumbling of structural industrial links, the unfavourable ecological situation stipulate a sharp increase of the losses of agricultural and food products, generally lead to such negative consequences as the rise of the deficit of protein and vitamins in the food ration, pollution of food with metabolic products of pathogenic bacteria, including with carcinogens.

Ecologically safe packaging materials are created by modifying traditional polymers with polyfunctional additives, which perform the functions of structure formers, plasticizers, antibiotics, relaxants of internal stresses, and stabilizers. Scientific bases of creating packaging materials for foodstuffs have been developed. Additives providing the production of materials, which are biochemically resistant to the impact of microflora and aggressive media of food productions, are introduced into the composition of their base. Methods of regulating the processes of mass transfer and distribution of structure-forming additives

4 INTRODUCTION

along the thickness of the packaging materials with the aim to form an optimal structure and operational properties have been developed.

Fundamental works have been carried out on the development of packaging materials and coatings based on various polyolefins, ftorlons, epoxy polyesters and other polymers of mesomorphic structure, which provide for the production of packagings with polyfunctional properties.

Special attention is given to the development of scientific principles of creating self-degrading packaging materials with regulated service life and biodegradation upon disposal.

Valuable characteristics of these materials are determined by the necessity of combining the biocide properties with respect to foods in storage with the ability to be degraded in soil under the action of microflora.

1 Methods and Technology of Preserving the Nutritive Value of Food

1.1 The nutritive value of foodstuffs

Special attention should be paid to the control of losses of food products in their processing, storage, transportation and sale. This could not be done without scientifically grounded rational application of polymer materials, which are used to preserve food products. In this connection, it is necessary to consider the specific properties of both food itself and of polymers in contact with it (packaging materials, containers, various coatings).

To preserve food well, it is necessary to know which of its specific properties should be retained until it reaches consumer's table, bearing in mind the concepts "healthy food" and "tasty food" from the viewpoint of food biochemistry. Man can not exist without food. It provides the organism with necessary substances for growth and is a source of energy, which is transformed into heat required for the bodily functions of the human organism.

For a long time, the only index of food value was its caloric value. Energy is constantly consumed throughout human life to maintain the normal body temperature, for mental and physical work. Usually, a human in normal condition should consume an amount of food, which corresponds to energy consumption by its caloric value.

The amount of energy required for the human organism, internal consumption including, is determined in special chambers used to measure the amount of heat evolving in the lying position, during physical or mental activities. Naturally, depending on the intensity of work, the amount of energy evolved and, therefore, the requirement of its replenishment at the expense of the caloric value of food would be different.

The human organism receives energy mainly due to oxidation of food. Actually, food is not assimilated completely, and its real caloric value is slightly less than the amount of heat evolved in its oxidation. Carbohydrates and fats burn almost completely. In oxidation of carbohydrates and proteins, the energy evolved per 1 kg is $16.8 \cdot 10^3$ kJ; of fats, $37.8 \cdot 10^3$ kJ.

The basis of food are proteins, fats and carbohydrates. All foods essential for health consist of proteins, fats and carbohydrates, and also of some other components. For the organism, it is not the same if it receives these calories by consuming carbohydrates or fats. The latter are more difficult to assimilate, and they come to the blood flow later. Proteins are indispensable for the organism. Apart from the fact that they replenish the energy consumed, they provide for the restoration of expended cells and tissues and ensure the development of the human organism at the young age.

POLYMERS FOR PACKAGING AND CONTAINERS IN FOOD INDUSTRY

Food does not only deliver energy for work and is required for us to move, think, for the heart to pump blood through the body, to maintain normal body temperature; it also provides material for the incessant regeneration of tissues and cells. The most active constituent parts of cells and tissues, consisting of proteins, are to be regenerated first of all. Various types of proteins can be distinguished. They perform various functions in the organism.

Proteins of connective tissues fasten muscles and bones in tendons. Proteins, of which muscles consist, are capable of contracting and stretching, in accordance with orders from the brain, to bring into motion organs of the human body. Proteins of the blood deliver oxygen required for oxidation of tissues (without which the human organism is not capable of maintaining life and performing work) and pick up the waste product, carbon dioxide. Cutaneous coverings, hairs, mucous envelopes also consist of proteins.

Of no less importance in comparison with the above is the regulatory function of proteins. They regulate the vital processes in cells and organs. From the point of view of chemistry, these proteins catalyze and regulate chemical processes. Digestion is also one of these processes.

Proteins in question are enzymes. Participating in the regulation of vital processes, protein molecules are subjected to changes, as a result of which they lose their valuable properties. Thus, it is necessary that the replacement for spent proteins come with food. Therefore, sources of energy – fats and carbohydrates – are interchangeable. From the viewpoint of their energy functions, they can be replaced with proteins. Proteins themselves are indispensable, as they are valuable for the organism not only as an energy source but also as building material for cells and as catalysts and regulators of biochemical processes.

Therefore, the value of food products is determined not only by their caloric value but also by the content of protein substances. The hierarchy of food products by this parameter differs from that obtained from comparison of foodstuffs by their caloric value.

Consider the protein content in different food products consumed in this country, %:

Soy	34.9	Rice	7.6
Dry pea	23.8	Cow milk	2.8
Cheddar cheese	23	Potato	2.0
Boiled hen	20.6	Cabbage	1.8
Beef	17	Carrot	1.2
Cod	16.5	Butter	0.6
Mutton	15.7	Margarine	0.3
Pork	15.2	Marmalade	traces
Eggs	12.8	Sunflower oil	none
Wheat flour	10.5	Sugar	none

Food products can not be characterized by their caloric value alone. Despite the high caloric values of sunflower oil and sugar, the human organism would not function in a normal way, however large amounts of these high-calorie products are consumed. It is imperative that food of man contains fats, carbohydrates and proteins. In the human organism, protein molecules break up to form smaller molecules, amino acids. Amino acid molecules can be of different size and structure. Their common feature is the presence of amino and carboxyl groups in the molecule. It has been established that amino acids required for the vital activities of the human organism can be divided into nonessential and essential. Non-essential amino acids can be synthesized by the human organism from fragments of molecules. Essential amino acids can not be synthesized and should be obtained with food.

Apart from proteins, fats and carbohydrates, the human organism requires vitamins. They are essential. Certainly, vitamins can be injected or swallowed in pill form. But the most useful method is to introduce vitamins with food. As molecules of amino acids are fragments of large molecules of proteins, so vitamins are ready-made fragments of the most important enzymes regulating the metabolism. Vitamins are divided into water-soluble and fat-soluble. For example, vitamin C – ascorbic acid – belongs to the former. The human organism is not capable of synthesizing it, despite its comparatively simple chemical structure, probably, because the mankind has been almost always surrounded by natural sources of vitamin C, which occurs in almost all fresh vegetables and fruits. This vitamin is present in dill (0.15%), horseradish (0.2%), red pepper (0.25%), black currant (0.3%), winter pine needles (0.22–0.28%), dry briar (1–5%) and in other vegetables, fruits and greens. Ascorbic acid is unstable and is easily destroyed in cooking, drying, preservation and in long-time storage in air. Deficiency of vitamin C in food causes a severe disease, scurvy.

One of fat-soluble vitamins is widely known vitamin A, which is involved in the synthesis of rhodopsin required for good vision and is contained in fish liver oil, carrot and other products. Vitamin A occurs mainly in products of animal origin. Its highest amount is in beef liver and cod. The liver stores 90% of all vitamin A in the animal and human organism. Good sources of this vitamin are hen's and quail's eggs, butter, dairy cream and sour cream. Though plant products contain no vitamin A, some of them (carrot, red mountain ash, sea buckthorn berries) contain a large amount of carotene – up to 10 mg per 100 g product. Under the action of carotenase in the intestines, carotene is converted to vitamin A. Carotene is a rather unstable, readily oxidizable compound. For this reason, chopped vegetables and greens should not be left unused for a long time, as carotene in them would lose biological activity. Greens and vegetables should be cut immediately before a meal. As carotene does not dissolve in water but dissolves well in fats and oil, it would be assimilated better if an edible fat is added to vegetable dishes. For instance, grated carrots could be dressed with mayonnaise or sour cream.

The daily requirement of vitamin A is 0.5-0.7 mg for children aged from one up to ten years old; 1 mg for older-age children and adults; 1.25 mg for pregnant women; 1.5 mg for breastfeeding women.

For persons whose work is associated with a heavy load on the organs of vision, those who work evening or night shifts or have contact with substances causing irritation of the mucosa of the eye, the daily intake of vitamin A should be increased 1.5-2-fold.

Deficiency of vitamin B can cause polyneuritis. Vitamin B_2 (riboflavin) is required for normal sight. The absence or deficiency of PP (nicotinic acid) leads to a heavy disease, pellagra, and vitamin B_2 contains the element cobalt required for the vital activity of the cells.

Thus, besides fats and carbohydrates, the human organism should receive with food a set of essential amino acids, vitamins, cellulose for normal functioning of the gastrointestinal tract. But even this is not sufficient for food to be wholesome and to contain all elements required for the vital activities of the organism. The important components are salts, which contain such elements as potassium, sodium, calcium, phosphorus, fluorine, as well as various trace elements in small amounts. Sodium is an important constituent of the blood and together with potassium is required for the normal functioning of the nervous system. Human bones consist of calcium phosphate. Adenosine triphosphoric acid is a kind of an energy storage device in the human organism. Phosphorus-containing nucleic acids code for the program of building up and operating each cell of the organism and, therefore, the program of constructing the entire organism, i.e., heredity. Protein molecules also include sulfur. The absence of iodine makes impossible the normal functioning of the thyroid gland. Iron is a component of blood hemoglobin. Fluorine is required for the normal state of the teeth.

However, food should be not only wholesome but also tasty and even attractive to the eye. By its appearance and aroma, it should cause a reflectory secretion of the substances, which contribute to the digestion and assimilation of food. Therefore, a broad diversity of gastronomy should not be reduced to carbohydrates, fats, amino acids, vitamins and salts. In spite of the seeming rationality of introducing a certain amount of nutrients into the organism, the human can not live on tablets or powders of even the most perfect and wellbalanced diet. It is not by chance that even at the dawn of cosmonautics, when each extra gram of load in the spaceship significantly complicated the mission, even then cosmonauts did not swallow powders or pills consisting of amino acids, carbohydrates, fats and other components. The taste, smell and appearance of food is not a caprice but an essential requirement of the human organism. The diversity of taste hues can be reduced to a combination of four main gustatory properties: sour, sweet, bitter and salty. The edges of the tongue are the most sensitive to sour taste; the base, to bitter taste, the tip, to sweet and salty tastes. All acids have a sour taste. Cooking salt, as is known, possesses a salty taste. However, salts of most metals are not salty in taste, but bitter. In general, the relation between the chemical structure of a substance and its taste has been investigated to date obviously insufficiently. Peptides have a taste, which depends on which amino acids they consist of. High-molecular-mass compounds, whose molecules are characterized by molecular-mass magnitudes of the order of tens and hundreds of thousands are, as a rule, tasteless. This pertains to polysaccharides and polypeptides (proteins). As for the taste of amino acids, the sweet ones are D-tryptophane, D-histidine, D-phenylalanine, L-alanine, glycine (in decreasing order). L-Tryptophane, L-phenyl alanine and the so-called L-isomers are bitter. D-Alanine, D- and L-aspartic acids, D-glutamic acid are tasteless or have a very weak taste.

Food products are sometimes artificially flavoured, for example, to add a sweet taste. Herewith, it is known that sugar is not the very sweet substance. Saccharine, for instance, is 400–500 times as sweet as sugar, but is not assimilated by the human organism.

Glycine (an amino acid possessing a sweet taste) is agreeable to the taste and wholesome. It is widely used in production of soups, condiments, marinades; it softens a bitter or salty taste and eliminates an unpleasant off-flavour of some products. Glycine is present in large amounts in fish, prawns, molluscs.

D-Tryptophane and maltol are used to enhance sweetness. Addition of maltol in the amount of 15 ppm makes it possible to decrease the consumption of sugar by 15%.

Preparation of food – boiling, broiling, roasting, fermenting, pickling, junketing etc. – is accompanied with complex chemical reactions, as the result of which a large amount of various volatile compounds are formed. Their content in food is negligible but the flavour of food changes depending on the ratio of these compounds in the steams.

In individual cooking, it is easier to follow the preservation of useful substances, taste, colour and smell. It is far more difficult to bring the valuable properties of food to the consumer's table, when food products are mass produced in meat-, milk- or food-packaging plants; when these products should be preserved in the process of production, transportation and storage in refrigerators, in the process of selling them up to the moment when the food gets into the human organism.

Considering the problem of food preservation, one should not be abstracted from the fact that foodstuffs are involved in the common closed process of interaction of the human organism with the environment. The late 1970s and early 1980s witnessed the formation of a new interdisciplinary science of food and nutrition, *trophology* (the Greek word " $\tau \rho \phi \phi$ o"

means "aliment"). Trophology combines together the earlier disconnected links of the chain and various aspects of the science of food, such as the distribution of nutrient substances in the cell or in the organism; the mechanism of the transfer of nutrient substances along the food chains; the role of trophological processes in the circulation of substances in the biosphere; evolution of species and evolution of the biosphere. As far as the life of each organism and the maintenance of life depend essentially on the equilibrium between the synthesis and decomposition of nutrient substances, the biosphere can be considered as a troposphere, and all organisms as links of the planetary food chain, a "food hierarchy" forming a closed circle. The new science of trophology should combine together the earlier scattered links of this chain.

An integrated view of the trophological process made one to approach the evaluation of food in a new way. While it was believed earlier that the organism needed as much food as it consumed, it was not food in general that was meant but the nutrients assimilated by the organism - amino acids, carbohydrates, fatty acids, vitamins, essential salts. All the other components of foodstuffs were considered to be an unnecessary ballast, which complicates the bodily functions of the human organism. At present, one of the fundamental conclusions of trophology is that, apart from the main flow of nutrients, four more flows come to the organism. One of the most important flows is that of physiologically active substances formed in the stomach and in the intestines. The so called hormones and mediators are implied.

If one takes account of all hormone-producing cells in the human gastrointestinal tract, the result would be the largest endocrine gland in the human organism. This gland secretes hormones, which control the essential metabolic functions and assimilation of nutrients. Three other flows are formed in the gastrointestinal tract with the participation of bacterial flora. The bacterial flora is required for the human organism and higher animals to exist. Only the proportional ratio of all four flows creates normal conditions for the vital activities of the organism. The so-called "ballast" substances, which until recently were to be withdrawn from food to make it closer to an "ideal" meal, are in reality also required for the human organism. On removal of, e.g., food fibres - cellulose or lignin - from food, the cholesterol metabolism is disturbed, which can cause stones in the gall bladder or else a stomach or intestinal disease. Therefore, ballast-free elementary diets are applicable only in the case of some defects of the enzyme systems.

1.2 Methods and technology of preserving food products and raw materials

Large amounts of food products in the CIS countries are lost at the stages of raw-material production, processing, transportation, storage and, finally, sales. A considerable amount of potatoes, milk, grain, meat perishes as the result of losses in harvesting, transportation and storage.

The use of polymer materials makes it possible to preserve the quality and significantly reduce the losses of food products.

At the stages of raw-material production, polymer materials are mainly used in growing the agricultural produce, in raising and sagination of domestic animals. One of the important areas of polymer use to increase the crop yield is the presowing treatment of seeds. It consists of spraying the seeds with a polymer suspension, which includes nutrients, trace elements, plant-growth regulators, insecticides and other biologically active substances.

The basis of film-forming compositions are water-soluble polymers with specific

physicochemical and physicomechanical properties and the possibility of providing a hydrophilic/hydrophobic balance in the system. Protective films reliably protect seeds from the action of low temperatures, from premature germination under unfavourable conditions. The properties of the coatings are programmed depending on the biological peculiarities of plants. This is achieved by chemical modification of a polymer (e.g., polyvinyl alcohol) in the process of film formation and polymer structure change both at the molecular and supramolecular levels.

The climatic conditions in many cases make it necessary to grow fruits and vegetables under coverage. The major factor, which limits the possibility of growing vegetables, berries, fruits and other crops in unprotected areas is insufficient warmth. The temperature conditions can be adjusted using hothouses, hotbeds, covers and other cultivation constructions. Only these agricultural constructions can significantly improve the temperature conditions in the plant-vegetation zone. These constructions prove economically efficient if fabricated using polymer-film materials, which, though inferior than silicate glass with respect to life time, are cheap, transportable and easy to erect. The major factor causing the ageing of polymer films is solar radiation in the ultraviolet and infrared regions of the spectrum.

Application of polymer-film materials in cultivation constructions in agriculture is rather efficient; however, it creates the problem of utilization of used films. Upon use and loss of consumer properties, the polymer film retains mainly a two-dimensional structure. It pollutes the ground and is not degraded or assimilated by the environment for about 80 years. Therefore, the use of polymer films in agriculture leads to the necessity to solve the problem of utilization of used films or their transfer into a state in which they are assimilated by the environment, i.e., to control the polymer degradation processes. Photochemical degradation of polyolefins leads to the formation of CO2 and H2O, which are assimilated by plants. Some organometal compounds, as well as complexes of variable-valence metals with dialkyl dithiocarbamate (usually used as thermostabilizers of plastics), catalytically degrade products of photooxidation of polymers, e.g., hydroperoxides, in storage. Besides, complex compounds of metals are capable of absorbing the light energy. In the interaction of organometal compounds with hydroperoxides, the so-called Norrish reactions occur. Depending on the content of sensitizers (the Scott-Gilid system), polymer is subjected to degradation or the system exerts a thermostabilizing action on it. The Scott-Gilid system is easily introduced into polymer together with other additives and pigments.

The requirements imposed on photodegradable polymers used in agriculture and in industries are rather stringent. They should have a guaranteed service life, good mechanical properties, be rapidly and completely degradable after the induction period, polymer degradation products formed should not be toxic, polymers should not change their properties in storage, the polymer composition should be easily processable into items produced. These polymers should not be expensive.

Polymer films used to fabricate cultivation constructions strongly warm up (to a temperature of $60-85^{\circ}$ C) in places of the contact with the supporting structures of the frames. Film covers on hothouses are subjected to the action of negative temperatures, which in the North regions reach -19 to -40° C. Calculations show that in the North-West and Central European regions of the Russian Federation, in the Urals, in Western and Eastern Siberia, in the Ukraine, Belarus, Uzbekistan, Latvia, Estonia, Moldova, Turkmenistan the thickness of films from light-stabilized polyethylene for covering hothouses should be no less than 0.15 mm. Research showed that harvest quality and crop yield are practically the same at different UV transmission degrees. Therefore, films with UV radiation-absorbing

stabilizing additives can be used when growing most agricultural crops in hothouses. The most widespread type of film used in hothouses in Western and Eastern Europe and the USA are polyethylene films. This is due to their comparatively low cost, simple production technology, possibility of manufacturing wide formats and other advantages, e.g., the simplicity of introducing various modifying additives. For these purposes, polyethylene of specials brands was manufactured.

Of film materials used for growing agricultural produce under coverage, mention should be made of heat-resistant polymer films for disinfection of hothouse grounds with live steam. This is the basic method of disinfecting hothouse grounds. It was invented in Holland, but a Russian development is also available. According to this method, to increase the efficiency of steaming (which kills all kinds of pests of agricultural crops) the ground to be steamed is covered with a polymer film, which contributes to faster and deeper steaming. The ground is covered with the film, which is fixed with sand bags along the perimeter. Live steam at a temperature of 115–120°C is fed under the film. The ground and the film is acted upon with steam of a slightly lower temperature (90–100°C). One cycle of steaming provides for holding the film at a high temperature (90–100°C) for 12 h, and then for another 12 h to cooling.

Apart from growing fruits and vegetables in hothouses, films are also used to arrange small-size covers – cultivation constructions whose size does not allow the handling of plants and harvesting inside these constructions. Such constructions include skeleton covers for growing plants, tunnel film covers; to some extent, special perforated films are also applicable. In the latter case, the supply of heat to the ground in the spring and the warming-up of the soil are much greater than in an open plot. A wide-format film $20-30 \mu m$ thick is also efficiently used for covering sown crops and plantings without wireframes (the edges of the film are buried into the ground 5-10 cm deep). The thin film does not prevent the plant growth and provides for the hothouse effect required. Only perforated films are used for this purpose. Though skeleton-free coverings are less efficient as compared with skeleton ones, their total economic efficiency is higher.

Removal of the films should be done by hand and is associated with pollution of the environment, in connection with which a number of problems arises. One of the efficient ways of solving them is to use films with a given lifetime, upon expiry of which the films are degraded under the action of light, moisture and other natural factors to produce forms assimilable by the environment. Degradation of the film on skeleton-free covers can start in 20 to 70 days, but this time strongly depends on weather conditions.

Besides the described methods, polymer films are successfully used to make winter coverings of fruits and berries, hay etc.

Mulching is an agrotechnical technique to prevent evaporation of moisture and formation of a soil crust, to maintain an optimal temperature of the soil and to suppress the growth of weeds. Film mulching is used both in unprotected grounds, and inside film-covered hothouses and tunnels. Polyethylene films are the most widespread; they can be transparent, semi-transparent, non-transparent, light- and heat-reflecting (white and aluminiummetallized). The greatest warming-up of the soil is observed in mulching by lighttransparent films, the use of which ensures a 40–50% greater heat supply to the soil than in an open plot. Semi-transparent films decrease the soil warming-up from 50 to 80–90% depending on their integral light transparency. Reflecting films smooth the total amplitude of soil temperature variations owing to the warming-up during the day and the delayed cooling during the night. Coating the soil with cuts from metallized polyethylene films reduces the extent of damage (owing to the illumination of the low side of the leaves) of undersized vegetable plants by some species of insects (aphids, flea beetles and bugs). Black mulching films detain evaporation of moisture, but prevent penetration of solar radiation to the soil surface. Film mulching enhances the biological activity of the soil; herewith, the amount of microorganisms in the soil and their activity change, the illuviation of readily soluble nitrogen fertilizers from the soil is delayed.

Mulching of the soil in cultivation constructions can be done most rationally by used films for covering hothouses, as well as secondary polyethylene films.

Mulching by light-reflecting films in winter hothouses, when there is not enough light, has become widespread. It improves the illumination conditions and increases the early harvest by 15-25%. Additional illumination at the expense of the light reflected by the film accelerates the ripening of strawberries, salads, kohlrabi in winter hothouses. A black film for mulching, PE-157 brand SM (GOST 10354-82), was developed and is manufactured in the CIS countries. Light-transparent photodegradable films PE-108-70 and PE-108-71 are used for short-time mulching of vegetables and berries, potatoes and other crops. Besides them, CIS industries also manufacture film materials of other types used for mulching in unprotected and protected ground. In agriculture, fibre- and tissue-reinforced films are used for growing and storing vegetables and fruits. By their optical characteristics, they are slightly worse than polyethylene non-reinforced films. Reinforced films can be used at a temperature from -60 up to +60 °C. They are mainly used for erecting cultivation constructions of protected ground (greenhouses, hothouses, coverings). The service life of the constructions is in this case longer (as compared with non-reinforced coatings), especially in regions with increased wind and snow loads. Buildings and constructions from reinforced polymer film materials are conditionally divided into three types: awnings, pneumatic constructions, skeleton constructions.

Skeleton constructions are distinguished by large reliability and do not require the use of high-strength air-impenetrable materials. They are best of all to be used for growing and storing horticultural produce. Skeleton-film warehouses and storages of horticultural and other agricultural produce can be built quickly (3–5 days) and require no large capital investments or additional lighting. If it is necessary to make the premises darker, two-layer coatings are used, the lower layer of which is light-impenetrable and which are fabricated from, e.g., polyethylene filled with carbon black.

Foodstuffs can be protected from harmful substances getting into them by correctly using the protective properties of polymer materials. It is important not only to grow a heavy crop, to harvest it, but, which is especially important, to preserve it (not only from the point of view of quantity, but also quality) up to the very moment of food consumption.

The problem of food preservation interested the man since long time ago. It was solved differently at different times by different peoples.

The problem of food preservation emerged in connection with the need to store up food reserves for oneself, one's own tribe, equipping an expedition, equipping an army etc.

Subsequently, formation and development of microbiology made it possible to lay the scientific foundation under various technological techniques of food preservation. It proved that the vital activities of microorganisms, which contribute to the spoilage of food, manifest themselves under conditions of a certain temperature regime, certain humidity, absence of substances aggressively interacting with substances from which microorganisms consist, etc. If the conditions do not correspond to those required for the development of microorganisms, the latter perish or their vital activities are temporarily stopped and, therefore, the process of food spoilage stops, too.

A widespread technological technique of preserving food products is drying. The

technique is based on the fact that most chemical processes determining the vital activities of bacteria occur in an aqueous medium. Removal of water leads to the inhibition or interruption of chemical reactions contributing to the development of microorganisms and accompanying food spoilage.

In cells of fresh products, the food substances are, as a rule, in solution. In the course of drying, the concentration of this solution increases until it becomes so high that the solution can not be absorbed by the cells of various microorganisms any more. At the extent of drying, corresponding to the above situation, a food product can be stored without deterioration of its quality for a long time. The content of moisture in it should be observed not to be higher than a certain limit: 12-14% for dried vegetables, 18-25% for dried fruits. The smaller is the moisture content in the product after drying, the greater the guarantee of its preservation is, the less the conditions for spoilage are.

However, the lower the moisture content in a dried product is, the more complicated and, therefore, expensive the process of drying is. Besides, some substances useful for the organism can be destroyed in the process. During the drying, water is evaporated from particles of the product and vapours formed are carried away. Drying is performed most often using hot air, which, being a heat carrier, communicates a heat energy to water molecules. Owing to the acquired energy, water molecules overcome weak physical and physicochemical bonds and pass from the product into the vapour. The higher the temperature of the air is, the more water molecules pass into the vapour, i.e., into the heated air.

The moisture capacity of the air is different at different temperatures. This method is used to increase the storage life of fruits, vegetables, milk, meat, fish and other foodstuffs.

In drying apples and pears, mainly early varieties are used. Primarily fruit drops are dried. It is best to dry fruits of one variety. In the summer, fruits usually dry up in 3–4 days. Before drying, fruits are washed. Washed fruits are examined to cut the damaged parts, the cores are excised and the fruits are cut into slices not more than 1 cm thick. Small fruits and pears can be cut into two or four parts.

A method of preserving products by drying at low temperature – freeze-drying – is of an ever increasing importance at present.

The process of sublimation (removal of moisture at low temperature, when a product is preliminarily frozen) can be greatly accelerated by removing water vapour by direct pumping out (evacuation), condensation of vapours on a chilled surface, absorption of vapours by hygroscopic substances. The use of the method of freezing for preserving food products revealed the phenomenon of structure breakdown of plant and animal tissues by growing crystals of ice. To avoid this undesirable phenomenon accompanied by the loss of a number of useful specific properties of food products, the following technique is used. Products are chilled so rapidly that ice crystals have no time not even to grow but to be formed. Products prepared for freeze-drying are frozen and placed into a chamber, from which the air and vapours are pumped out. If pressure in the chamber decreases from the initial magnitude (of the order of 760 mm Hg) down to 1-1.5 mm Hg, water could not be in a liquid state under these conditions and passes from the solid state (ice) into the gaseous state by omitting the liquid state, i.e., it evaporates. Transition of a substance from the solid state into the gaseous state by omitting the liquid state is called sublimation. The vapours formed are pumped out by vacuum pumps, and water is gradually removed from the frozen product. It dries at a low temperature.

One of the main requirements to drying, as to the other preservation methods, is the maximum preservation of the nutritive value of food products. Numerous studies of the biological and nutritive value of food products subjected to various methods of drying have

been carried out with this in mind. The results of studies convincingly showed that the best integrity of food products and their nutritive value is provided for by the method of freeze drying. This refers equally to products of both plant and animal origin.

Removal of water from a food product – drying – is a forced measure, which is due to the necessity to inhibit the chemical reactions occurring in storage. After the storage, the product should restore its initial properties and the initial content of moisture. Therefore, the reversibility of the drying process is essentially determined by the capability of the dried product to swell again in contact with water. A relative increment (with respect to the mass of the dry product) of mass in swelling is called the extent of swelling. The extent of swelling of freeze-dried mutton was 3.5%, whereas that of heat-dried mutton only 2%. In other words, meat after freeze-drying increased its mass 4.5-fold in 40-45 min, after which no increment was observed: all water, which the freeze-dried meat was capable of absorbing, was absorbed. The process of water absorption is also observed in heat-dried meat. However, this process was slower than in freeze-dried meat, and it was completed only after 2.5-3 hours of swelling. The mass of heat-dried meat, after it absorbed the maximally possible amount of water, increased only three times. This difference in the swelling of freeze-dried and heat-dried mutton is explainable by the denaturation of proteins and thickening of muscle tissue. Freeze-dried meat, being boiled after 12 months of storage, preserved its culinary and organoleptic properties. The caloric value of freeze-dried mutton is 3.5 times as large as that of raw meat. Heat-dried meat is close to freeze-dried meat by its caloric value. However, by its organoleptic properties (taste, smell, appearance) freeze-dried mutton is much better than that of heat drying. Fat on freeze-dried mutton chops does not differ from raw meat. A heat-dried duck broth is usually turbid and has an unpleasant taste. A broth from freeze-dried meat tastes good and has the specific flavour of a duck broth.

A similar pattern is observed in comparison of freeze-dried and heat-dried fish. Thus, proteins of freeze-dried meat of pike perch preserve their properties better than proteins of heat-dried meat. Only insignificant changes in the composition of its proteins were observed during the storage of freeze-dried pike-perch meat. The specific composition of liver oil determines its oxidation susceptibility. After a 12-month storage of freeze-dried meat of pike perch, vitamin B₁ was totally preserved. The extent of swelling of freeze-dried pike-perch meat reached an equilibrium value in 30–40 min and was 3.5. The swelling equilibrium of heat-dried meat was established only in 3 h and was characterized by the swelling extent of 2.2. It is known that the culinary properties of heat-dried meat of pike perch leave much to be desired. But the broth from freeze-dried pike-perch meat, obtained by boiling for 15-17 min, has a good taste and flavour. Similar results were also obtained in comparative studies of heat-dried and freeze-dried fillet of common carp. The caloric value of freeze-dried common carp meat proved almost five times as high as that of raw meat.

Freeze drying involves freezing of a product. However, it should be noted that freezing of food products is of independent significance, not necessarily associated with drying of a product. Chilling of foodstuffs can be used both for drying and with the aim to inhibit the spoilage process without freezing the product itself. This goal is pursued in storing products in refrigerators. But cold can also be used for freezing products with the aim of their further processing. In the former case, products should be kept intact during the chilling, having in mind not only mechanical damage but also the integrity of cell viability. Herewith, the biochemical processes continue in the products stored but, naturally, at a slower pace. The metabolic processes in, e.g., chilled fruits and berries are active, they breathe and ripen. Freezing of foodstuffs is accompanied by significant changes in their tissues and cells. The

moisture in them freezes and turns into crystals of ice, which grow and partially destroy cells. Moisture freeze-out is, in turn, accompanied by dehydration of the liquid part, in which the nutrient materials of the cells are dissolved. During the unfreezing of such products, the moisture formed in thawing of ice crystals can not be absorbed by the cells, which underwent irreversible changes. Unfrozen products abundantly ooze juice. However, undesirable phenomena associated with the growth of crystals in freezing could be avoided. For this purpose, the process of freezing should be very quick not to let ice crystals to be formed. The matter is that for crystals, in particular, ice crystals, to be formed, their constituent molecules and atoms should be arranged in space in a strict order relative to one another. The lower the temperature, the larger the viscosity of the liquid is. Therefore, if the cooling is performed quickly, then, starting from some temperature, the rearrangement of the structure has no time to be completed. The temperature is so low that a crystal should have formed, but the structure remains the one corresponding to the liquid state. Molecules can not move in space, but perform vibratory heat motions. There are no crystals and, thus, no irreversible changes of the cells and tissues of frozen products take place. Therefore, to obtain a higher quality of frozen products in modern refrigerating industry, the freezing process should be performed quickly, with an intensive removal of heat, at as low temperature as possible. In rapidly frozen products, the cell envelopes mainly remain unbroken. Therefore, there is no juice oozing out after such products are unfrozen. Modern freezing installations usually provide for the coolant temperature within -25 to -35° C. A product is frozen to -18° C and is stored at this temperature. During the storage, periodic temperature increases should be avoided, as an increase of even several degrees is accompanied by the recrystallization of ice, growth of separate crystals with all ensuing consequences.

To manufacture high-quality fast-frozen products, it is necessary to provide for the freezing of manufactured semi-finished products in a fast freezer, storage of frozen products in a refrigerator chamber of the plant, transportation of the products in refrigerator railroad cars or refrigerated road vehicles for their sales. In shops, these products should also be stored in distribution refrigerators or chambers. After purchasing rapidly frozen produces, consumers should keep them in refrigerators, without allowing even for a short-time thawing. Manufacturing of high-quality frozen products is associated with expenditures for complex refrigerating equipment. However, when comparing various methods of foodstuff preservation (sterilization, drying, pickling, marinading, addition of preservative agents), it should be stated that in fast frozen foodstuffs the quality of the product – preservation of taste, culinary merits, vitamins, aromatic substances – proves the highest.

At present, the domestic industries manufacture a broad range of fast-frozen foodstuffs. They include various kinds of fruits and vegetables, as well as products of a high degree of doneness, such as vegetable, meat-and-vegetable and fish first and second courses, fruit juices.

The process of freezing proceeds the most qualitatively and efficiently in special fastfreezing machines. Storage and transportation of frozen products requires their packaging in hermetic and moisture-proof containers. If these conditions are not observed, during the storage of frozen products in chambers at a temperature of -15 down to -18° C the moisture will be sublimed into the air bathing the products. The moisture that passed from the product to the air is condensed at cold pipelines, walls, ceilings as frost. The layer of accumulating frost prevents the transfer of heat from the freezing product to the coolant. Thus, nonhermetic or moisture-permeable packagings will cause the loss of weight of a freezing product, deterioration of its quality and worsening of heat-exchange parameters. Usually, loose frozen products are poured onto tables covered with tin-plate sheets and packaged into 16

containers. Above, we mentioned the necessity to maintain the temperature of a frozen product constant both in storage and in transportation, as otherwise ice-crystal growth will take place with the ensuing consequences.

Fish meat is in most cases less prone to deterioration when frozen by traditional methods. However, during the storage in refrigerators evaporation of moisture takes place, which is accompanied by the penetration of ice crystals into the tissues. To prevent losses and quality deterioration of fish products, a new cryotechnology for processing polymers from aqueous solutions was developed. A protective coating is formed on fish products without any additional energy expenses. Two types of food coatings, Polyol-1 and Polyol-2, were developed. The second coating contains preservative agents for the inhibitory action on microflora and a structure former to produce an elastic transparent coating with a long lifetime. Fresh fish is to be coated, which makes it possible to preserve additionally large quantities of a valuable product lost at the stage of preliminary freezing. The process for the Polyol-1 protective coating was implemented at the Gurievrybprom Production Enterprise of the Kaspryba All-Russian Industrial Association for long-term refrigeration storage of frozen fish.

An incorrect choice of material for containers and packagings of frozen products, the same way as an incorrect packaging of a product, can render null all professional actions of sorting, calibration, washing, cleaning, cutting, chopping, freezing and other process operations.

Considering the methods of preserving food products, we can not but dwell on one of the classical methods - preservation by heat. Vegetables for preserves, the composition of which includes, besides vegetables, only water and some salt and sugar for good taste, are subjected to washing, calibration, cleaning, cutting and blanching. The caloric value of such preserves is not high, but they keep almost all valuable properties of preserved vegetables. This applies to their taste, flavour and food value. Most vegetable natural preserves are sterilized by heating above 100°C. For instance, green peas are preserved, when their grains are green, soft and sugary. Usually at this stage of ripeness, their grains contain 5-7% sugar, 20-30% vitamin C, proteins and mineral substances. Prepared grains of green peas are blanched at 90-98°C for 3-4 min, after which the grains are immediately cooled to avoid overcooking. Green-pea grains thus prepared are packaged into tin-plate or glass containers, and a hot filling is poured in. The filling consists of sugar (2-3%) and salt (2-3%) dissolved in hot water and should be filtered before use. Sealed containers are subjected to sterilization by heating to kill microorganisms, which cause spoilage of the product. In industrial conditions, such a sterilization is performed in autoclaves - hermetically closed cylindrical steel boilers. The higher the sterilization temperature is, the sooner the sterilization is completed, i.e., the less time is required to kill microbes. However, too high sterilization temperature can lead to a deterioration of the quality of the preserves: darkening of the product, an unpleasant flavour etc. These changes are usually due to undesirable chemical reactions between the components of the product at too high temperatures, which do not occur at lower temperatures. The sterilization temperature is determined by the resistance of microbes to high temperatures, which essentially depends on the acidity of the sterilized product. Usually, bacteria not forming spores perish during the boiling. Sporulating bacteria perish only at a long-time heating up to 110-120°C. In an acidic medium, e.g., in tomato or sorrel puree, bacteria do not develop. However, in such products spoilage is due to molds and yeasts, which perish in boiling. Products with a low acidity are sterilized at temperatures of 112-120°C. Large containers are heated up slower, low flat cans are heated up faster than high ones.

Besides temperature, size and shape of cans, the sterilization time is also determined by the consistence of the product. The more densely the product, e.g., paste, fills a can, the more time is required for the necessary temperature to be established in the middle of the packaging. Besides the thermal conductivity of the contents of the packagings, the sterilization time is also determined by the thermal conductivity of (iron, glass or polymer) containers, as well as the initial temperature of cans. Therefore, its own regime of thermal sterilization should be chosen for each kind of preserves and each type of cans, based on the above conditions.

1.3 Technology of preserving the quality of foodstuffs in manufacturing, transportation and sales

In production of foodstuffs, of great importance for preventing losses and spoilage, as well as corrosion of food equipment is the use of antiadhesion coatings.

An optimal coating for baking rye bread was developed and is used at the St.-Petersburg Bread-baking Plant No 12. Besides the economy of oil, the antiadhesion coating saves a considerable amount of flour, eliminates expenses for oiling and cleaning of molds, facilitates the application of automatic machines and, which is of no small importance, enable increasing the quality of baked goods. In molds free of burnt deposits the required temperature is easier to maintain, losses of bread are much smaller, the work of oven operators is much easier. Antiadhesion polymer coatings are applicable in other branches of food industry, e.g., in meat and dairy industry. Some components of the equipment in food industry, in particular, shelves and racks for storing and ripening cheese are made from wood and have a number of disadvantages: they are short-lived, are characterized by a highly labourintensive service due to stickage of cheese and integrated sanitation treatment, during which wood warps. Besides, labour-intensive process operations can not be mechanized in this case. Shelves and racks can be fabricated from cheep carbon steel coated with a polymer coating, which should possess a low adhesiveness to foodstuffs and necessary physicomechanical and sanitation properties. The most important requirements to such coatings in operation are the stability of antiadhesion and physicomechanical properties, protection of the metal equipment from corrosion under conditions of high humidity within the temperature range of 10 up to 80°C. Material with the required properties can be produced by targeted modification of non-critical and physiologically harmless polymers, e.g., highdensity polyethylene (HDPE). To eliminate the cracking of HDPE-based coatings in their operation in aggressive moist media, HDPE was modified by polyethyl siloxan PES-5, as the result of which HDPE was stabilized, and the antiadhesion properties of the coating improved.

The most labour-intensive operations in fabrication of molded meat products include dislodging of a product from the mold and the subsequent cleaning of its surface. Interlaying materials – cellophane and cooking parchment paper – are used inefficiently to provide for the separation of a product and a mold. Animal fat is used for greasing the molds in production of meat loafs, as the result of which a deposit is formed on the molds. The quality of the products and the sanitary condition of the production shop deteriorate in this case, the molds should be subjected to systematic cleaning, which makes difficult the mechanization and automation of the processes. All these drawbacks can be eliminated by using antiadhesion coatings.

In the process industries of the agroindustrial complex, of great significance is the protection of equipment from corrosion. In this respect, it is difficult to overestimate the role of antiadhesion coatings which by their sanitary characteristics are permitted to be used in contact with food products. The problem of corrosion is very significant, though achievements in this field are quite a few, the domestic developments including.

One should take into account the losses of manufactured food products in storage, transportation and sales by commercial enterprises. Various compositions for the protective coating of food products are known. Thus, a composition was invented, which protects cheeses from drying and molding. A composition for coating sausages and a method of producing a casing on them were proposed. A composition for applying a protective coating on fish and fishery products was also developed.

The most promising method of long-time preservation of the nutritive properties of food products is their low-temperature preservation. However, a considerable amount of weight of a product is lost in freezing and subsequent storage due to evaporation of moisture, the quality of a product deteriorates, oxidation of lipids and denaturation changes of proteins occur. One of the rational ways to retain the quality of products is to create coatings impermeable for oxygen and moisture on their surface. For this purpose, aqueous solutions of biologically inert polymers, e.g., polyvinyl alcohol (PA) are used. PA acquires water resistance in the process of film formation at low temperature. During the freezing of the polymer–solvent system, as the result of a phase transition accompanied by an abnormal increase of its volume, PA undergoes mechanochemical transformations (cryolysis). Cryocracking of macromolecules is accompanied by the emergence of active cryolyzates, whose interaction leads to the formation of insoluble spatial structures.

The topicality of the problem of using advanced polymer materials determined the necessity of international forums – exhibitions and symposia dedicated to this problem. The cost of a packaging was on average 8% of the cost of product. There is a tendency in European countries to sell foodstuffs in packagings convenient for preparation of food in microwave ovens.

Great attention is paid to the process evaluation of the packaging systems from the environment-protection point of view. Among the main tendencies of the packaging business in the USA, it is necessary to note the development and commercial production of ecologically pure packagings, a decrease of pollution of the environment. There is a tendency to move from multi-layer to single-layer packagings, e.g., single-layer bottles from polyethylene terephthalate (PET), which are easy to identify and reprocess. Packagings are used, in which deep-freeze dishes can be warmed in microwave ovens (PET). Thus, Gorton's place fish sticks into a packaging, which is equipped with elements from metallized PET film above and below. The elements are susceptible to the absorption of microwaves, which leads to the effect of a crunchy crust. Special attention is paid to the use of renewable resources (wood, plants). In this respect, of interest is the packaging material based on ethrol, which under certain processing conditions can be transferred to a liquid-crystalline state. Packaging in a film material in liquid-crystalline state is rather promising.

Polymer packaging materials found wide use throughout the world, Russia including. Expanded production of polymer film materials is restricted only by deficit of the initial materials. For this reason, it is possible to organize production of polyisoprene hydrochloride-based polymer films with good sanitation parameters, in contact with fats including, which easily yield to two-dimensional strain and shrink after orientation at 70°C. The initial materials are polyisoprene (whose output reaches several million tons per year), HCl and methyl chloride (which should be subjected to recuperation), a small amount of sorbic acid (used as food stabilizer at present). The method of producing a film-forming material based on polyisoprene hydrochloride was developed well back in 1960s.

Multilayer films became widespread in the world practice as packaging materials. The first domestic multilayer film for packaging non-fat food products was a film from polyethylene and cellophane, which was improved and found widely used for packaging food products (not of increased fat content). Cellophane is produced from naturally renewable raw materials, is biologically harmless (at a corresponding control of production), possesses the barrier properties, which significantly deteriorate when it is moistened. A disadvantage of cellophane is its incapability of heat sealing, which greatly worsens the packaging process of food products. A combination of these materials produces a film heat-sealed material with high barrier properties. However, as the inner layer is polyethylene, this material can not be in contact with fatty food products. Progress in the development of multilayer film materials in this and other countries was accompanied by the emergence of multilayer films with different combinations of paper, foil, various polymer films and binders. The problems one comes across in this case are pollution of the environment and interaction of a foodstuff with the packaging. Regularities of the interaction of a foodstuff with the packing and with the environment are being revealed. The most important processes of this king are penetration of oxygen, water vapours, light and carcinogens from the atmosphere into a foodstuff through polymer films. Substances contained in the foodstuff can get to the environment through the packaging. These processes are undesirable.

In the recent years, the use of the vacuum freeze drying of food products has become more widespread, and the popularity of this method has increased. Production of foodstuffs by this method has both positive and negative aspects.

The positive aspects include the high quality of these products; by their nutritive and gustatory properties, they are comparable only with natural deep-frozen products (studies by E.I. Kaukhcheshvili). A positive quality is also the capability of long-time storage (up to 1 year and more) under non-regulated conditions of the environment. A drawback is the high cost of vacuum freeze preservation; as shown by B.P. Kamovnikov, average reduced costs for the removal of moisture from an object of vacuum freeze drying exceed similar expenses for heat drying 15-20 times.

A quite natural and justified idea would be to reduce the costs of preserving freezedried products several times without decreasing the high consumer properties. Calculations show that, though this is difficult, this problem is quite realizable technically: to solve it, the freeze-drying process should be performed not in a vacuum, but at an atmospheric pressure. This would, first, make it possible to exclude the expensive and energy-intensive vacuum equipment from the process. Second, at an atmospheric pressure heat-and-mass transfer could be intensified (especially at the final stage of drying) due to the convection of the drying agent, which is out of the question under vacuum conditions. In other words, for production of daily-consumed freeze-dried products the vacuum freeze-drying should be replaced with atmospheric freeze-drying (AFD).

In a general case, the process of preservation by the AFD method includes the following major operations: sorting and treatment of raw materials, freezing, removal of moisture by freeze drying at negative temperatures, cold and hot completion of drying to a given final moisture content, prepackaging and packaging of the dried product. The properties of the preserved products crucially depend on the condition of raw materials and the quality of performing each of the above operations. Herewith, the preservation process has its peculiar features for each particular kind of product, depending on the properties of raw materials and requirements to the final product.

It should be pointed out that materials dried by the AFD method are rather hygroscopic and have a large specific surface of the dry carcass.



Figure 1 Classification of objects of drying.

For this reason, long-term storage without reduction of quality can be possible only in a reliable hermetically sealed packaging. With any other conditions equal, the duration and quality of storage are basically determined by the quality of packaging. For instance, the use of metal tin-plate cans or multilayer metallized films for fabrication of packages and the filling-up of these containers with a dry product with gaseous nitrogen makes it possible to provide for the storage of plant products in the off-season period.

As the preservation by the AFD method is a sufficiently complex process, and the preserved products are usually intended for long-time storage, the requirements to the initial raw materials are high. The nutritive value and vendibility, structural mechanical properties and admissible terms of storage, the temperature level of processing and duration of individual process operations – all these are largely determined by the properties of the raw materials. Along with the diversity of the chemical composition of various food products, they are characterized by one common property: they contain a considerable amount of water.

As objects of processing (including by preservation by the AFD method), products are classified by their physical nature into objects of animal and plant origin and sea foods. By their consumer properties, a separate group is endocrine / enzyme raw materials, which are usually not used as a source of food, but are an essential source in production of medicines and biologically active substance.

A classification of objects of drying is presented in Fig. 1. The purpose of products is taken as the first-rank classification criterion. Two large groups are singled out here – food-stuffs and raw materials for production of medical preparations and biostimulants.

The second rank of classification is chosen to be the characteristic of dividing the objects by their physical nature. Individual groups of objects of drying singled out at the second-rank level differ significantly by their composition, physicochemical and other properties (Table 1.1). For this reason, the possibility of using methods of vacuum or atmospheric freeze drying for their preservation and the choice of drying regimes should be decided upon separately for each group of products close by their properties.

A complex interaction of these components with water and with one another forms the properties of food products. The amount of water in a product also determines the conditions of its storage, which would not reduce its quality.

Meat used for preservation by the AFD method should conform to a number of requirements. Cartilages, large vessels and connective tissue are removed during the trimming in the preparation of meat for drying. These inclusions considerably differ by their heat transfer properties from muscle tissue, their presence would lead to nonuniform drying, worse rehydration of the dry product, would reduce vendibility and gustatory qualities of culinary products made using the dry product. A high content of fatty tissue is inadmissible. The melting temperatures of animal fats are rather low (e.g., beef fat, $32-52^{\circ}$ C; pork fat, $28-48^{\circ}$ C; chicken fat, $23-38^{\circ}$ C). For this reason, at the stage of residual moisture removal (completion of drying) fat can melt and fill free pores, which would sharply increase the duration of drying and formation of non-drying inclusions (lenses) in the depth of the specimen. Besides, at the stage of storage of dried meat the oxidative transformations of the lipid fractions can drastically deteriorate the organoleptic parameters of the product. These changes can be the largest in pork and poultry meat, as fats of these kinds of meat contain many unsaturated fatty acids.

Product	Water, %	Proteins, %	Fats, %	Carbo- hydrates, %	Fibre, %	Ash, %	Energy value, 100 g/kJ
Pasteurized milk	88.5	2.8	3.2	4.7	-	0.7	243
No fat curd cheese	77.7	18.0	0.6	1.5	_	1.2	360
Common beef	71.7	20.2	7.0	-	-	1.1	602
1st category hens	61.9	18.2	18.4	0.7	_	0.8	1008
Hen's eggs	74.0	12.7	11.7	0.7	-	1.0	657
Azov-sea carp	75.3	18.4	5.5	-	-	1.0	506
Potato	75.0	2.0	0.1	19.7	1.0	1.11	374
Cabbage	88.5	1.3	0.1	7.0	1.2	1.0	138
Mushrooms	88	1.8	0.8	1.1	1.5	0.4	79
Apples	85.6	0.4	_	11.3	0.6	0.5	192
Black currant	85	1.0	_	8.0	3.0	0.9	167
Apricots	86	0.9	-	10.5	0.8	0.7	192
Plums	87	0.8	_	9.9	0.5	1.3	180
Bulb onion	86	1.7	-	9.5	0.7	1.0	180

Table	1.1
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The requirements to the raw materials intended for preservation by AFD are satisfied the most by meat of young animals. The muscle fibres of this meat are more thin and elastic, meat possesses a relatively lower mechanical strength, the content of fat in it is small.

An important factor in producing a high-quality product is the dependence of the properties of meat not only on the tissue and chemical compositions, but also on the depth of autolysis. According to the obtained recommendations, meat after a 3- or 4-day holding at $2-4^{\circ}$ C should be used for preservation by freeze drying.

When choosing the AFD regimes for milk and dairy products, it should be taken into account that the properties of milk proteins change in heating and freezing. Thus, in freezing (down to temperatures below -10° C), the colloidal properties of milk proteins change, their solubility decreases. Milk fat in the milk mass is distributed in the form of balls up to 5 μ m in diameter, each of which is enclosed by an envelope containing a protein complex. In the contact of lipid fractions with oxygen of the air during the AFD process or in storage of a dry product, the product can rancidify and suffer a deterioration of taste. For this reason, when packaging dry milk and dairy products it is necessary, as in the case of packaging dry meat products, to use hermetic vapour- and light-impenetrable containers filled with inert gas. Products prepared from no fat milk are more resistant.

22 POLYMERS FOR PACKAGING AND CONTAINERS IN FOOD INDUSTRY

Milk sugar (lactose) is close by its nutritive value to common beetroot sugar. However, a larger content of reducing sugars in milk and dairy products (e.g., in mare milk, up to 7%) creates conditions for sugar-amine reactions in storage of dried products. For their maximum inhibition, it is necessary to remove moisture from dairy products in the process of drying up to 2-3%. In practice, during the preservation by the AFD method this condition is achieved by drying dairy products in air convector heaters (furnaces) at temperatures of $40-50^{\circ}$ C upon completion of the moisture removal by the ice–vapour phase transition.

Freeze drying of milk, curd, many fermented milk products makes it possible to preserve maximally the high quality of the product produced. And for such products as, e.g., acidophilic paste and Mechnikov's sour milk, it has no alternative.

The recent decade is characterized by an increased production of new kinds of products based on combinations of meat raw materials with proteins of plant and animal origin. Among protein preparations used for partial replacement of meat raw materials, compositions used the most are milk proteins (sodium caseinate, milk-protein concentrate etc.) as well as soy proteins (soy isolate, soy concentrate, soy flour and grits). Numerous experiments have proved that a rational level of the substitution of protein for meat raw materials is from 10 up to 30%, depending on the kind of protein used.

Introduction of rehydrated protein preparations into the meat system raises the stability of the dried meat's lipid fraction to oxidation and increases the storage times, raises the resistance to thermal denaturation, provides for the balance of the amino acid composition, improves the organoleptic properties of culinary products prepared from reconstituted dry products. An especially important fact is the possibility of drying and freeze drying of meat products with protein additives at a higher temperature as compared with meat products containing no protein fillers. A temperature increase could be $5-6^{\circ}$ C without the loss of quality, which enables saving energy and in some cases using a simpler equipment.

Milk and soy proteins are widely used at present for enrichment of meat products. Milk proteins are added into chopped meat as sodium caseinate. The substitution of sodium ions for calcium available in milk has a positive effect on the increase of solubility of the protein and imparting it with the properties of a water-binding and fat-emulsifying component.

Precipitation of casein with whey proteins yields preparations containing all milk proteins, the so called coprecipitates with up to 80% protein in the dry residue.

Processing of soybeans to obtain food proteins is performed in several directions, which enables production of soy flour and grits containing about 50% protein: soy concentrate (produced from soy grit, from which soluble carbohydrates are removed and protein passes into an insoluble form), the content of protein up to 70%; soy isolate (highly purified protein preparations without taste and smell), the content of protein up to 90%. Integrated studies of the chemical composition of some kinds of protein preparations show that all protein preparations are characterized by a high protein content and a low fat content.

Soy protein preparations contain essential vitamins and mineral salts.

A comparative analysis of the amino acid composition indicates that plant protein preparations are characterized by a lower content of sulfur-containing amino acids as compared with proteins of animal origin. However, when soy proteins are used in a complex with proteins of animal origin (muscle protein, caseinate, blood plasma) their biological activity increases due to the mutual enrichment with essential amino acids.

In the freeze drying of eggs, a mixture of egg white and yolk (a melange) or only white is used. A promising procedure is the use of eggs for preparing products with a whipped structure – meat, milk or fruit souffle, which are then preserved by the AFD method.

The presence of various enzyme systems in eggs leads to the development of autolytic

changes in their storage, the general tendency of which is similar to the autolysis process in animal tissues, so dietary or fresh eggs are used as the initial product. According to the operating standard, the former are the eggs that come to the consumer no later than 7 days from the day of laying and not kept in solutions. Fresh eggs are those that were kept at a temperature of +2 to -2° C for no more than 30 days.

Along with animal and poultry meat, fish is an essential source of complete proteins; proteins of fish meat are easily assimilated by the human organism. Constituents of fish meat are basically represented by proteins, lipids and water. The chemical composition of tissues is rather inconstant and depends on the fish species, age, time of capture etc. Thus, the relative moisture content is on average from 53 (eel) up to 81% (cod, pike perch); protein substances, 10 up to 24%. Variations are even larger in the fat content – from 0.2-0.4 up to 30%. Fatty meat contains less water than lean meat. However, the total content of water and fat in the fish body remains practically always a constant value close to 80%.

For atmospheric freeze drying, only the meat of fish with a minimum amount of fat could be used, as it could be oxidized both during the drying and in storage. We should note that, owing to a high degree of unsaturation, fish fats are easily oxidized; herewith, some of these products can be toxic. As the result of postmortem processes, fish meat undergoes significant physicochemical changes. The initial stage of rigor mortis is characterized by intensive glycolysis of glycogen, accumulation of lactic acid in muscles and a pH decrease. The further development of the processes finally leads to contraction and tension of muscles. With the course of time, rigor occurs owing to the further irreversible protein changes, determined as maturation and autolysis. Meat becomes more tender.

Sea is also a source of other valuable foodstuffs (e.g., prawns, crabs) and raw materials for medical industry (various algae). Freshwater reservoirs are habitats of such a valuable source of protein and biologically active substances as chlorella. These objects can be successfully preserved by the AFD method. The qualitative indices of dry semi-finished products conformed to the imposed requirements.

A characteristic feature of all plant products is a large water content, 66–96%. The main carbohydrates of fruits and vegetables are sugars, starch, cellulose and pectin substances. Studies of plant-origin products show that the chemical composition of even one species changes depending on the extent of ripeness, variety, growth conditions etc.

Fruits and vegetables contain all known vitamins, except vitamins B_{12} and D (calcipherol). Vitamins C, A (as provitamin A, carotene), vitamin K occur in largest amounts. Plant products are the main source of vitamin C. The change of its content in the food ration due to freezing, freeze drying and subsequent storage of the dry product is (together with the organoleptic indices) an essential criterion of quality of the entire preservation process.

Vitamin C is easily destroyed by heating and under the action of oxygen of the air. Thus, in the presence of oxygen of the air it breaks down already at a temperature of 50° C. This should be taken into account when choosing the temperature regime at the stage of completion of the drying, as well as when choosing the design of the device for AFD.

Fruits and berries contain a considerable amount of sugars, from 7-9% (black currant, garden strawberries, apples) up to 20-25% (dog-rose, grapes). In vegetables, the content of sugars is usually at a level of 4-6%. Sugars are represented by glucose, sucrose and fructose, the quantitative ratios between which are different for each kind of product. Changes in the properties of sugars in the course of the process have a strong effect on the quality of the ready-made product. The action of high temperatures is inadmissible, they can contribute to the caramelization of sugars, induce reactions of melanoidin formation as a consequence of the interaction of sugars with amino acids. As the result, browning of the product

takes place. Note that plant products with a significant sugar content, e.g., bananas, are practically unsuitable for preservation by the AFD method.

Fruits and vegetables contain 0.2-3% of cellulose, which is mainly used for construction of envelopes and cell walls. The composition and content of the cell walls determine the mechanical properties of tissue. Cellulose is characterized by a high chemical resistance. Preservation of fruits and vegetables by the AFD method usually envisages the destruction of cellulose – the preparation of purees and pastes, comminution.

The pectin substances of plant-origin products include complex polysaccharides. In fruits and vegetables, they are 0.1-2% of the total mass of a product. Significant amounts of pectin are in apples, quince, plums, apricots. Pectins have the property of forming stable colloidal solutions. The condition of the pectin substances in a dry product largely determines the degree of its rehydration.

As shown by the experience of preserving a broad assortment of fruits, vegetables and berries by the method of vacuum freeze drying, the ultimate choice of this or that variety with the aim to obtain a high-quality dry product can be made only based on the experimental check in each particular case. It was found that particular varieties of plant-origin products, good by their initial quality parameters, were unsuitable for preservation (due to the loss of shape in drying, instability in storage, bad rehydration). In full measure, this is also valid in the case of the AFD method.

The AFD method has a great potential for preserving flavouring/spicy plants added to foods for flavour and to excite appetite. Many savoury herbs in the form of spices have a strong bactericidal action. In the European part of Russia, these are widely used dill, parsley, parsnip, coriander (cilantro), peppermint and estragon (tarragon). Leaves of these plants contain various aromatic oils, vitamin C, provitamin A, biologically active substances.

1.4 Application of chemical preservatives in food industry

1.4.1 General information on chemical food preservatives

Chemical preservatives are synthetic chemical substances used for slowing down or preventing undesirable changes in foodstuffs and technical products of biological origin caused by microorganisms – bacteria, molds, yeasts.

Chemical food preservatives include sulfurous anhydride and some salts of sulfurous acid; benzoic, sorbic, propionic acids and some of their salts; methyl, ethyl and propyl esters of *para*-oxybenzoic acid. Hexamethylene tetramine; formic, boric and salicilic acids; formaldehyde, hydrogen peroxide have not been used lately in most countries.

Preservatives make it possible to increase the storage times of ready-made products and raw materials, as well as prevent spoilage of raw materials in processing. Preservatives are usually used when other methods are not possible.

Application of chemical preservations is restricted as, being toxic for microorganisms, they are harmful for man and animals. Therefore, they are used at very small concentrations, harmless for higher organisms and man.

In food industry, chemical preservatives are used mainly in combination with heating, freezing, drying, irradiation etc. Their actions add up.

The method of treating a product with preservatives depends on the kind of product and its condition. Liquid and comminuted products are usually thoroughly mixed with the preservative. Lump products are subjected to surface treatment, e.g., by immersing a product into a solution or by sprinkling it with a solution. Treatment of the surface of a product is especially expedient when there are no microorganisms inside it.

Preservatives cause damage to microbial cells, reversible (bacteriostatic or fungistatic action) or irreversible, as a consequence of which cells die (bacteriocidal or fungicidal action).

At a bacteriostatic action, microorganisms remain alive, but are not capable of propagation. If they are transferred to a favourable medium, propagation becomes possible again. However, microorganisms gradually die even at a bacteriostasis, depending on the concentration and duration of action of a preservative. In practice, bacteriocidally acting substances differ from bacteriostatic ones only by a greater pace of microbial die-off.

The rate of bactericidal action increases with the increase of the concentration of a chemical substance and temperature.

Bacterial cells can develop, propagate, produce toxins only under certain conditions. Bacteria, e.g., are sensitive to pH of the environment. A significant change of pH leads to a change of the surface amphoteric structures of the cell and, owing to this, to a disturbance of cell equilibrium followed by cell death. In particular, the osmotic exchange between the cell and the environment is disturbed. In some microorganisms, a pH decrease causes an activation of the ribonuclease autolytic system, which is unfavourable for cell viability.

Bacteria, with few exceptions, can develop in media with pH 4.2–9.4; yeasts develop in a more narrow pH interval (4.0-6.8); and mold fungi, within even broader pH limits (1.2-11.1).

Many preservatives of acidic type are more efficient at low pH, as a major part of them are in a non-dissociated form (Table 1.2).

Preservative acid	Dissociation Non-dissociative (real) part, %, at				art, %, at p	pН	
	constant	2	3	4	5	6	7
Sulfurous	$1.7 \cdot 10^{-2}$	37	5.5	0.55	0.04	0.001	0
Bromoacetic	$2.05 \cdot 10^{-3}$	83.0	32.8	4.65	0.48	0.049	0.0049
Salicilic	$1.06 \cdot 10^{-3}$	90	49	8.6	0.94	0.094	0.0094
Formic	$1.77 \cdot 10^{-4}$	98.3	85.0	36.1	5.35	0.56	0.056
p-Chlorobenzoic	$9.3 \cdot 10^{-5}$	99	91	52	9.7	1.06	0.107
Benzoic	$6.46 \cdot 10^{-5}$	99.3	93.9	60.7	13.4	1.52	0.15
p-Oxybenzoic	$3.3 \cdot 10^{-5}$	99.7	96.8	75.2	22.3	2.94	0.30
Acetic	$1.8 \cdot 10^{-5}$	99.8	98.2	84.7	35.7	5.26	0.55
Sorbic	$1.73 \cdot 10^{-5}$	99.8	98.3	85.2	36.6	5.46	0.57
Propionic	$1.4 \cdot 10^{-5}$	100	99	88	42	6.7	0.71
Dehydroacetic	$5.3 \cdot 10^{-8}$	100	100	95	65	15.8	1.9
Bisulfite	$1.02 \cdot 10^{-7}$	100	100	99.9	99.0	90.7	49.5
Boric	$7.3 \cdot 10^{-10}$	100	100	100	100	100	100

Table 1	.2
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Owing to this, molecules of an acid can penetrate into microbial cells, whereas penetration of ions into cells is impossible or barely possible.

As the dissociation constant of a preservative acid decreases, even at a neutral or weakly acidic reaction, the number of non-dissociated molecules, which guarantee its action, increases. The weaker a preservative acid, the closer the pH can be to the neutral point; the preservative action of the preservative does not decrease. Non-dissociating preservatives, e.g., esters of *para*-oxybenzoic acid, are relatively independent of pH and can change at the neutral reaction.

1.4.2 Mechanism of action of chemical preservatives

The mechanism of action of chemical preservatives on microorganisms has been little studied to date.

Common methods of determining the inhibitory doses of chemical preservatives can not reveal the mechanism of their action. They can only establish the concentrations, at which the propagation of microorganisms slows down. In practice, it is believed that a preservative is efficient if it prevents the growth and propagation of microorganisms.

The probable mechanism of action of chemical preservatives on microorganisms, proposed comparatively recently and accepted at present, is presented below.

Compound	Probable effect
Cationic and anionic surfactants	Disturbance of cytoplasmic cell membrane. Denaturation of enzyme protein
Phenols, chlorophenols, naphthol sulfonates, cinnamic acid	Disturbance of cytoplasmic cell membrane. Reaction with genetic-mechanism proteins
Fatty acids, alcohols and high-molecular- mass aldehydes	Disturbance of cytoplasmic cell membrane. Competitive inhibition of enzymes by low-molecular-mass acids
Chloroacetic acid	Effect on the cell wall. Competitive inhibition
Benzoic acid, <i>p</i> -chlorobenzoic acid, <i>p</i> -oxybenzoic acid and its esters	Effect on the cell wall. Competition with coenzyme for apoenzyme
Salicilic acid	Effect on the cell wall. Competition with nicotinamide adenine dinucleotide. Competition with amino acids used by enzyme
Boric acid	Reaction with phosphorus metabolism enzymes
Sulfur dioxide, sodium sulfite, sodium bisulfite	Reaction with aldehydes formed in dissimilation of carbohydrates. Reduction of S–S bonds in enzyme protein
Chlorine, chloramines, nitrogen tri- chloride, peroxides, nitrates and other oxidants	Breakdown of sulfhydryl groups in enzyme proteins. Breakdown of sulfhydryl groups in genetic-mechanism proteins.
Ethylene oxide and other epoxides	Reaction with carboxyl and other active groups in enzyme protein
Fluorides, fluorosilicon compounds and fluoroborates	Reaction with prosthetic groups of enzymes. Reaction with active groups of enzyme protein
Formaldehyde	Reaction with active groups of enzyme protein. Reaction with active groups of genetic-mechanism protein
Salts	Precipitation of enzyme proteins

Exchange between the bacterial cell and the environment is on the level of a limiting surface (the envelope); a number of differentiated protoplasmic structures, which create conditions required for active exchange of the cell with the environment, also occur here. Any substance violating this "topography" of the cell causes a disorganization of surface structures, which is equivalent to cell damage. In these cases, we observe bacteriostasis, or death, of the cell.

Under the action of chemical compounds, the metabolism in the microbial cell changes. Metabolism in any cell is inseparably linked with the activity of the enzymes.

The action of certain chemical substances on some enzymes can lead to the termination of preparation of nutritive material for assimilation, to the associated lack of nutrients and, therefore, to the interruption of the growth and propagation of microorganisms, i.e., to a bacteriostatic effect. If the stores in the cell are depleted, it dies. The total damage of certain enzymes, in particular, dehydrogenases, can lead to the cessation of the oxidative processes and associated processes of synthesis, i.e., to the termination of life. Depending on the reversibility or irreversibility of the reaction, the effect will be bacteriostatic or bacteriocidal.

Chemical substances, depending on their specific reactivity, can affect cell enzymes by interacting with the functional groups of an enzyme. The catalytic action of an enzyme is determined by several functional groups – sulfhydryl, disulfide, indole, imidazole etc. The breakdown or blockage of a group interacting with substrate or coenzyme leads to the cessation or deceleration of the catalytic reaction.

The mechanism of blockage of active groups of enzymes can be different. For instance, the sulfhydryl group is blocked via oxidation

$$2R \longrightarrow R \longrightarrow R \longrightarrow S \longrightarrow S \longrightarrow R$$

or substitution of hydrogen

$$R \longrightarrow SH + R'OH \implies R \longrightarrow S \longrightarrow R' + H_2O$$

Formaldehyde is characterized by a small selective reactivity. Depending on pH of the medium, it can block various functional groups: at pH 9.5, free amino acids; at pH 6.0, the imidazole group of histidine, at pH 5.0 and lower, formaldehyde is predominantly bound by amide and guanidine groups; it also reacts with indole and sulfhydryl groups.

The preserving action of sulfurous acid is also based on its capability of damaging the enzymes of the microbial cell. Substances capable of acting as reducers and oxidizers inhibit the activity of the enzymes. The enzymes containing the functional S-S group, on whose presence their catalytic activity depends, are inactivated by such reducing substances as SO_2 , H_2S , HCN, dithionate or HCOH. The S-S bonds are split to form HS groups.

Besides, sulfurous acids, by reacting with aldehydes formed in carbohydrate exchange, capture them and violate the normal metabolism in the microbial cell. Thus, acetaldehyde sulfonate formed in this reaction is not accessible to corresponding enzymes.

In this case, inhibition of activity of the enzyme system is achieved by blocking the substrate, which becomes inaccessible to microbial enzymes.

A possible explanation of the mechanism of inhibiting the growth of mold was proposed, proceeding from the supposition that sorbic acid is degraded to final products under the influence of mold enzymes by the type of the β -oxidation of fatty acids. At the same time, it was established that cyanide selectively inhibits oxidation of butyric acid to β -ketobutyric acid under the action of mold enzymes. Dehydrogenase, which catalyzes the conversion of butyric acid to crotonic acid, was not inactivated by cyanide, but the enzyme system catalyzing the conversion of crotonic acid to β -oxybutyric acid, was inactivated to tally. This means that α , β -unsaturated fatty acids accumulate in the medium; this accumulation inhibits the dehydrogenase system of molds. When sorbic acid is added to a food product, the final product of the reaction catalyzed by mold dehydrogenase is in excess, and dehydrogenase can not function.

At a high mold contamination, the concentration of all enzyme systems increases, owing to which the dehydrogenase activity can not be inhibited. Sorbic acid at a high mold contamination of a product is not active.

Chemical substances can inhibit an enzyme reaction by acting on a prosthetic group of the enzyme, by attaching themselves to coenzyme or else to the protein part of the enzyme in such a way that the bond between coenzyme and the protein component of the enzyme (apoenzyme) becomes impossible.

If a chemical substance is similar by its structure to coenzyme, it competes with coenzyme by capturing apoenzyme, as the result of which the enzyme is inactivated. This, in particular, is one of the mechanisms of action of benzoic acid and its salts, which compete with coenzyme for apoenzyme. The efficiency of action of benzoic acid in media with a lower amino acid content is higher than in food products, and under certain conditions nicotinic acid interferes into inhibition by benzoate.

Both inhibition and die-off of microorganisms can depend on various reasons, on one or several all at once. Therefore, when choosing a preservative, not only its concentration and time of action should be taken into account, but also the possibility of a simultaneous damage to a large number of vital mechanisms. To develop preservative formulae with an extended range of action, one should know the causes of microbial die-off under the action of a preservative.

As most preservatives possess a specific action with respect to various microbial species, and spoilage of food products is determined by a large number of microbial species, the development of combined compositions of preservatives has certain advantages. The additive action of two substances is possible owing to the fact that one substance, by acting on the cell envelope, facilitates penetration into the cell of another substance, or one of the preservatives decreases pH, and then the efficiency of action of the other preservative increases.

The efficiency of action of a composition made up from two or more preservatives can be increased by adding synergists, i.e., the substances, which possess no preservative action by themselves, but can enhance and maintain the preservative action of a preservative. Citric, tartaric and malic acids, as well as inorganic acids, their salts etc. can serve as synergists.

The action of double and triple combinations, consisting of a preservative (sorbic, formic, benzoic acids or *para*-oxybenzoic acid esters) and an antibiotic (nisin or tylosin, or both), was studied. A preservative is used to expand the antimicrobial range.

1.4.3 Characteristics and application of chemical preservatives

All methods of increasing the resistance of food products by using chemical preservatives have their advantages and disadvantages. First of all, taste can become worse, and the nutritive value can decrease. For instance, sulfurous acid degrades vitamin B_1 to a significant extent. Some preservatives are capable of disguising the true quality of a product, and a stale product can be passed off as a fresh product. For instance, formic acid possesses this capability with respect to meat products. Partially for this reason, preservatives of this kind are banned in most countries.

Benzoic acid (benzenecarboxylic acid; phenylformic acid) is present in most berries (0.5%).



Benzoic acid is a colourless crystalline substance, difficult to dissolve in water and rather easily dissolving in ethanol. It is used as a preservative; its efficiency increases in an acidic medium. The activity of benzoic acid against yeast fungi is higher than against molds.

Sodium benzoate (the sodium salt of benzenecarboxylic acid; the sodium salt of phenylformic acid) is an almost colourless crystalline substance.



Sodium benzoate

This salt dissolves well in water, worse in ethanol. The preservative activity is exhibited best of all in an acidic medium at pH lower than 5.0.

In studies of acute toxicity of benzoic acid and its sodium salt, LD_{50} for rats was 2700 mg/kg body weight; for rabbits and dogs, 2000 mg/kg body weight in peroral introduction.

In rats, prolonged feeding of food containing 0.5 and 1% of benzoic acid was found to have no harmful effect on their growth, fertility and life expectancy. No deviations from the norm were found in autopsy, either.

The dose causing no significant toxic effect in rats is 1% benzoic acid or sodium benzoate in food, which is equivalent to 500 mg/kg body weight per day.

Benzoic acid is used for preservation of food products usually at a concentration of up to 0.1%; sodium benzoate, at a concentration not exceeding this amount in terms of benzoic acid. Though the preservative action of benzoic acid is higher than that of sodium benzoate, the latter is used more often due to its better solubility in water. The solution should have pH lower than 4.5, then sodium benzoate is converted into free acid. Already at a 0.1% concentration, sodium benzoate is a strong preservative for many food products. It is efficient for acidic or slightly acidified products, such as fruit juices, marinaded vegetables.

Benzoic acid and its salts found use mainly for preserving products of plant origin.

In some cases, they are used for preservation of fish products. For instance, in Italy the use of benzoic acid and its sodium, potassium and calcium salts is permitted for processing of semipreserved fish products, caviar etc.

Ice containing 0.1% benzoic acid is known to be used for preservation of fish and fish fillet, and packaging of these products with ice containing 0.15-0.30% sodium benzoate enables their storage fresh for several days more than in a packaging with common ice. To avoid coagulation of fish surface layer proteins, pH of ice is maintained higher than 4.0. Besides, benzoic acid or its salts added at a concentration of 0.3% to a 5% solution of cooking salt with pH 4.0–5.0, into which a fish fillet is immersed for 2 min, considerably increases its storage time. Besides, the saline solution improves the taste of fish.

In many countries, benzoic acid and its salts are used for preservation of liquid eggs and egg yolk.

Sodium benzoate is considered to be a good preservative for oleomargarine. It does not affect the vitamin content.

Information on the use of benzoic acid or its salts for preservation of meat products is scarce. Preservation of meat salads and protective gelatin coatings for meat products by benzoic acid is known to be used.

There are indications that a 0.06% addition of benzoic acid increases twofold the stability of fresh sausages and other meat products. For their longer storage, it is recommended to add 4 g of a preservative mixture per 1 kg of sausage: 8.5 parts of benzoic acid, 8.5 parts of sodium benzoate, 8.3 parts of cooking salt. This method significantly inhibits the growth of all bacterial species.

In Russia, of products having a relation to meat industry, benzoic acid is allowed for preservation of food gelatin at a concentration of 0.07%.

Methyl, ethyl and propyl esters of *p*-oxybenzoic acid possess an ability to exhibit a preservative action in a neutral medium.



p-Oxybenzoic acid ester

In the formula, R is CH_3 , C_2H_5 or C_3H_7 .

These esters are colourless crystalline substances with almost no smell. All of them are hard to dissolve in water and are easily soluble in ethanol.

In acute experiments on mice, LD_{50} for methyl and propyl esters of *p*-oxybenzoic acid was more than 8000, and for their sodium salts 2000 mg/kg of body weight. In similar experiments for the sodium salt of ethyl ester of the same acid, LD_{50} was about 2500 mg/kg body weight.

In chronic experiments (96 weeks), methyl ester of *p*-oxybenzoic acid was introduced to rats with food in the amount of 2 and 8%. Animals given the feed containing 2% of the preparation did not differ from controls. In rats, which received feed containing 8% of the preparation the weight increase went down in the initial period of the experiment, and then levelled out. Histological studies revealed no significant changes in organs of rats. The same results were obtained in experiments with propyl ester.

The dose causing no significant toxic effect in rats is a 2% addition of each of the three esters to food, which is equivalent to a daily dose of 1000 mg/kg body weight.

Esters of *p*-oxybenzoic acid, mainly ethyl and propyl esters, and their mixtures were earlier rather broadly used in the West as preservatives for a number of confections – marzipan pastes, marmalades etc., mayonnaise, some fish semipreserves, caviar, especially crab preserves etc. Lately, they are not used in most countries.

In some countries, for instance, Norway, esters of *p*-oxybenzoic acid and its sodium salts are permitted to be used at a 0.05% concentration to increase the stability of some fish semipreserves, special types of cheese, as well as for surface treatment of cheeses. However, before paraffin treatment of cheeses, the preservative should be removed. Preservatives are introduced into compositions containing cellulose esters intended for the surface coating of salty meat products.

In Italy, ethyl and propyl esters of *p*-oxybenzoic acid are permitted to be used for preserving semipreserved fish products, caviar, mayonnaise etc. They are used instead of benzoic acid for preservation of meat salads and edible gelatin coatings for meat products. Ethyl ester of *p*-oxybenzoic acid at a 0.75% concentration makes it possible to store edible blood without its organoleptic properties changed.

Sorbic acid (1,3-pentadiene-1-carboxylic acid; α , γ -pentadiene-*a*-carboxylic acid; *trans*-2, *trans*-4-hexadiene acid) is represented by colourless needlelike crystals with moderately sharp smell:

СН₃СН=СНСН=СНСООН

Sorbic acid

The technical requirements to edible sorbic acid abroad (in the USA) are as follows:

Melting temperature (dry sample)	133.0-137.0°C
Titration (dry sample)	99.0-101.0% (w/w)
Water content	3.0-10.0% (w/w)
Heavy metal content	1 mg% (maximum)
Ash content	0.2% (maximum)
Transmission of light (5% methanol solution at 425 μ m)	95% (minimum) for a layer of 1 cm

Sorbic acid is soluble in cold water only slightly (0.15% at 20°C), but is much more soluble in hot water (3.8% at 100°C). The salts of sorbic acid are better soluble in water. The solubility of sodium sorbate in water is 32%, it does not essentially change depending on temperature within the range of 0-60°C. The solubility of potassium sorbate is more than 50% at 20°C, and calcium sorbate dissolves in the amount of 1.2% at 25°C.

The solubility of sorbic acid in various solvents at 20°C is shown in Table 1.3.

Solvent	Solubility, g/100 g solvent	Solvent	Solubility, g/100 g solvent
Glacial acetic acid	11.5	Ethyl ester	5.0
Acetone	9.2	Glycerol	0.31
Benzene	2.3	Cottonseed oil	0.58
Carbon tetrachloride	1.3	Anhydrous propylene glycol	5.5
Cyclohexane	0.28	25% sodium acetate	2.1
Anhydrous ethanol	12.9	15% sodium chloride	0.038
20% ethanol	0.29	Water	0.15

Table 1.3

Sorbic acid, having two unsaturated bonds in its structure, is a rather reactive compound. Its autooxidation leads to the formation of peroxides. It should be especially protected from the action of sunlight, otherwise the quality of the crystalline preparation worsens, which manifests itself in a melting temperature decrease, yellowing and rancidity.

Sorbic acid is used as an antimicrobial substance. It possesses a high activity against molds and yeast fungi and, to a smaller extent, against bacteria. Its optimal pH is 4.5. The fungistatic activity increases in the presence of acids and cooking salt. Sorbic acid is found in berries of mountain ash *Sorbus aucuparia* L.

In peroral introduction to rats, the lethal dose (LD_{50}) of sorbic acid was 10,500 mg/kg body weight.

Chronic experiments on rats were conducted for 1000 days on two generations of

animals. Rats were given feed, which contained 5% of sorbic acid. No deviations in weight increment and fertility from control animals were observed.

A dose causing no toxic effect in rats is 5% of sorbic acid in feed, which is equivalent to 2500 mg/kg body weight per day.

In subacute and chronic experiments on animals, sorbic acid was found not only to be non-toxic but possessed a number of favourable biological properties.

Sorbic acid is used to inhibit the growth of yeasts and against molding of fruit and vegetable juices, marinades, brines, smoked fish, flour confections etc., as well as to prevent damage of cheeses and margarine by mold. It is also used to impregnate packaging paper for food products.

Sorbic acid strongly inhibits the growth of molds and yeasts on smoked fish, if 0.05-0.1% of this preservative is absorbed by fish tissues during their soaking in a brine, which contains sorbic acid.

Usually, sorbic acid is used at a concentration of 0.02-0.2% of the weight of a product and has no influence on its colour and taste within these limits.

In meat industry, sorbic acid did not find wide use; however, there is information that it is used to inhibit the growth of mold on fermented sausages, for preservation of meat salads and edible gelatin coatings of meat products. A number of studies on the use of sorbic acid for increasing the stability of meat products yielded positive results.

An aqueous 0.5% solution of sorbic acid was used to remove mold from the surface of semi-smoked sausages. Wiping and rinsing of sausages in a solution of the acid made it possible to increase the storage time by 5-9 days. The loaves wiped with the solution and kept in it for 15 min could be stored 20 days more than those wiped with water. By adding 0.2% sorbic acid to sausage goods, their storage times can be increased by three days.

Treatment of the surface of raw pork and beef sausages, raw fish fillet, eviscerated poultry etc. by immersion for 0.1-2 min into an aqueous solution of 0.1-5.0% sorbicacid or its water-soluble salt and up to 0.2% antioxidant impedes microbial and oxidative spoilage.

The treatment of packaged fresh meat by sorbic acid and an antibiotic in combination with ionizing irradiation is also efficient in inhibiting microbial spoilage.

Deceleration of microbial growth in beef at $2^{\circ}C$, achieved by combining ionizing irradiation (10^{5} rad), oxytetracycline (1 mg%) and sorbic acid (0.1%), is shown in Table 1.4.

Table 1.4

Treatment	Tenfold population growth, days	
	yeasts and molds	bacteria
Control	>20	2-5.5
Irradiation	3.5-9.0	4-6
Oxytetracycline	3	7-8
Sorbic acid	>20	3-5
Irradiation + oxytetracycline	4	14
Irradiation + sorbic acid	8-17	8-17
Irradiation + sorbic acid + oxytetracycline	15-23	16-33

However, meat treated in this way is of much lower quality, dehydration is observed, as well as undesirable changes of colour and decreased flavour.

A promising way of increasing the storage times of eviscerated and cooled poultry carcasses in packagings is a two-stage treatment, which included acid hydration and use of sorbic acid. Part of a carcass is treated for 2 h in an ice-cooled solution of 2-substituted sodium phosphate. Herewith, pH < 5.5 is achieved on the surface. Then, after excess liquid leaks off, the carcass is treated with a hot (70°C) solution of sorbic acid. A mixture consisting of 70% propylene glycol, 20% water and 10% glycerine is used as a solvent. The sorbic acid concentration of 0.1-1 mg per 1 cm² of the product surface is achieved in 2–10 sec of drizzling. Control samples were spoiled in 5 days of storage at 7°C, while test samples were not spoiled in up to 18 days.

In some countries, it is permitted to add 0.1% sorbic acid and its sodium salts, which are used along with sorbic acid, into animal fats (except butter), margarine, egg yolk or a mixture of yolk and white. The solubility of the potassium salt in cold and hot water and water–alcohol mixtures can be considerably decreased in the presence of cooking salt and saccharose. They are active at pH 6 and lower.

Methods of commercial synthesis of sorbic acid have been developed in this country to date. Sorbic acid possesses a high efficiency with respect to molds and yeasts.

Sulfur dioxide (SO₂), sodium sulfite (Na₂SO₃), sodium metabisulfite (Na₂S₂O₅), sodium bisulfite (NaHSO₃) are soluble in water and are used as antimicrobial substances, as well as for preventing the browning of food products.

In acute experiments on mice at the intravenous injection, LD_{50} was 130 mg/kg body weigh for sodium bisulfite and 175 mg/kg for sodium sulfite.

Chronic experiments were performed in several groups of rats, 18-24 animals in each group. The daily ration given to rats for 1-2 years included sodium bisulfite in the amount of 0.0125, 0.025, 0.05, 0.1, 0.25, 0.5, 1 and 2% of the feed. No toxic phenomena were found in rats given 0.05% sodium bisulfite for 2 years.

Addition of sulfite to the feed at concentrations of 0.1% or higher caused growth inhibition in rats, possibly as the result of the degradation of thiamine in the feed.

The dose causing no significant toxic effect in rats is 0.05% sodium bisulfite in the feed, which is equivalent to 15 mg/kg body weight per day in terms of sulfur dioxide.

Sulfur dioxide found wide use for preservation of fruits, juices etc., but its application for products of animal origin is very limited. In Russia, this preservative is permitted to be added into food gelatin. The content of sulfurous acid in dry product should not exceed 0.1%.

In Norway, the content of sodium bisulfite in vacuum-packaged salt fish fillet is permitted to be up to 0.14%.

In England, sulfur dioxide is permitted to be used for preservation of raw sausages in the amount of 45 mg% of the weight of a product. In Scotland this addition of sulfur dioxide is permitted for chopped raw meat for the three summer months.

The treatment of sausage filling with sodium metabisulfite (in terms of 0.5 g SO₂ per kg of filling) increases its storage time at 5°C 2- or 3-fold. One of the undesirable phenomena in SO₂ treatment is, as was pointed out earlier, a considerable degradation of vitamin B_1 .

It has been proposed to treat the surface of hen and duck carcasses with metabisulfite. Carcasses are to be immersed into a bath with a 1% metabisulfite solution at a temperature of $63-66^{\circ}$ C and be held for 1 min. Then the carcasses are dried on a dressing rail and packaged into boxes. The treated carcasses are stored 3-5 times longer than controls at $8-10^{\circ}$ C.

A method was recommended to preserve gut raw material using a 0.5% solution of metabisulfite. The method is of particular importance for enterprises located in the thermal belt or those that prepare guts for long-time storage and transportation. Thus, a six-month storage of beef casings, bungs, rounds, hog and sheep casings as raw materials at a temper-

ature of 15–24°C and beef, hog and sheep casings as semifinished products at 29–40°C did not lead to any deviations from the norm during the subsequent use in sausage production.

To preserve non-food raw material and condemned materials (from non-infected animals), not processed by meat-processing plants for dry animal feeds in the period of mass livestock dressing, it is recommended to add dry sodium or potassium pyrosulfite ($(Na_2S_2O_5 \text{ or } K_2S_2O_5)$) in the amount of 2% of the weight of raw materials.

The same preservatives are proposed to be used for preservation of blood intended for feeding, which was earlier preserved by potassium oxide or diluted sulfuric acid in the presence of cooking salt. Defibrinated blood preserved using 1% potassium pyrosulfite to the weight of the blood can be stored for two months in the summer time at room temperature.

In gelatin production, sulfurous acid or hydrogen peroxide or both substances consecutively are usually used for preserving and whitening of high-quality broths intended for producing photographic gelatin.

For preservation of glue, a number of preservatives are used, including sulfur dioxide and sodium bisulfite.

Aliphatic acids. Fatty acids containing from 1 up to 14 carbon atoms are efficient inhibitors of molds. Propionic acid and its sodium and potassium salts prevent molding of bread and baked products. Salts of propionic acid found use in dairy industry, in particular in preventing molding on some types of packaged cheeses.

In meat industry, propionic acid and its salts found no use, because they deteriorate the organoleptic properties of meat products. However, it is possible that further research in this direction would find a possibility of using propionic acid and its salts for mold control in sausage production.

Formaldehyde, formic acid, salicilic acid, boric acid, borax, mono-, di- and trichloroacetic acids, hexamethylene tetramine (urotropin) etc. found application as food preservatives. At present, their use is banned in most countries, but in some countries hexamethylene tetramine, formic and boric acids are still permitted to be used for preservation of caviar and other fish products.

1.4.4 Methods for identification of preservatives

Quantitative determination of preservatives in products is made by gravimetric, titrometric, spectrophotometric, chromatographic and other methods.

A number of methods have been proposed for determining the content of sorbic acid in products. In most of them, the acid is isolated from a product by steam distillation. The distillate is used for the assay directly or is used to extract sorbic acid with ether to reduce the effect of minor impurities present in the distillate. In some cases, sorbic acid is isolated by extraction. However, this method is not applicable for fats and products containing large amounts of fat.

In the distillate or extract, sorbic acid can be determined titrometrically.

A simple method is the iodometric determination of sorbic acid in distillates or extracts from margarine, dairy products etc. The error of the method is $\pm 2.2-5.0\%$.

The widespread spectrophotometric method of determining sorbic acid in products is based on the ability of sorbic acid solutions to absorb light in the ultraviolet region of the spectrum. The light absorption maximum of the solution at pH 5.9 corresponds to the wavelength of $256 \,\mu$ m, and at pH 4.0, $262 \,\mu$ m.

The spectrophotometric method of determining sorbic acid, developed for cheese, was applied for other food products (bread, cakes, syrups, meat produces etc.).

Later, a more precise spectrophotometric method was recommended.

The content of sorbic acid in margarine was determined by the light absorption in the ultraviolet region of the spectrum at 260 µm.

The basis of one of the spectrophotometric methods is the reaction of sorbic acid with 2-methyl-mercaptobenzthiazol-p-ethyl toluene sulfonate (benzthiazol), which leads to the formation of a green product, whose light absorption is measured at a wavelength of 652 μm. Other chemical preservatives – benzoic, sulfurous, salicilic, formic, cinnamylic, propionic acids and a mixture of p-oxybenzoic acid esters - give no green coloration with benzthiazol and do not prevent the determination of sorbic acid. The method is recommended for determining sorbic acid in food products (cheese, butter etc.).

The method of paper chromatography was proposed for determining the content of preservatives in bread and baked products. Formic, propionic, benzoic, salicilic, sorbic, p-chlorobenzoic, p-oxybenzoic acids and p-oxybenzoic acid esters were identified.

For separation of p-oxybenzoic acid and some of its esters, methods of paper chromatography were also described, but they are lengthy and are inferior to thin-layer-chromatography methods in this respect.

The method of thin-layer chromatography was successfully used to separate p-oxybenzoic acid and its methyl, ethyl, propyl, isopropyl, butyl, isobutyl, hexyl, heptyl, octyl, nonyl, dodecyl, phenyl and benzyl esters. A mixture of 10% acetylcellulose and polyamide (1:1, w/w) was used as the stationary phase; a two-component system consisting of a hydrocarbon solvent and glacial acetic acid (50:10, v/v), as a mobile phase.

The separation of methyl and propyl esters of *p*-oxybenzoic acid was achieved on a thin layer of silica gel using a mobile phase from a mixture of pentane and glacial acetic acid.

A major part of the methods of determining sulfurous acid is based on its capability of being readily oxidized. There are volumetric and gravimetric method of determining sulfurous acid.

A comparatively exact and fast assay is the iodometric method of determining sulfur dioxide using formalin, which binds sulfurous acid.

1.4.5 Fat antioxidants

Under the action of oxygen of the air, fats undergo oxidative processes, which even at the early stages are accompanied by a decrease of nutritive value and subsequently lead to spoilage (unpleasant odour and taste, sometimes change of colour and consistency of fat).

The modern views on the mechanism of oxidative reactions of organic substances are based on the Bach-Engler peroxide theory and the theory of degenerate branched chain reactions by N.N. Semenov.

In accordance with the peroxide theory, the first product of oxidation of most organic and many inorganic substances are peroxides. When peroxide is formed, two atoms of the oxygen molecule still remain bound to each other. Therefore, in the oxygen molecule there is no complete rupture of bonds between atoms, which would require a large consumption of energy (117 kcal/mol). Thus, oxidation of organic substances via peroxide formation proceeds comparatively easily.

Peroxides were found even in freshly produced fats, because their oxidation begins already at the technological processing: in preparation of raw fat for rendering, during the rendering and in subsequent operations. Formation and accumulation of peroxides is greatly affected by the method of rat production. Comparison of the results of peroxide numbers'

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determination for pork rendered fats, obtained by various investigators, shows that the peroxide numbers of a fat rendered in an open heater are 0.013–0.035, and for that rendered on a centrifugal machine, 0.000–0.025.

The chemical composition of initial raw material and the changes that occurred in technological processing determine subsequently the rate of spoilage of fats in storage. The spoilage rate of a fat present in food products also depends to a great extent on these factors.

Many investigators, in particular, by the example of oxidation of fatty acid esters, have convincingly shown that at least at the first stages of oxidation all peroxide products formed are hydroperoxides

$$R_1$$
-CH-CH=CH- R_2
OOH

In the formation of hydroperoxide, oxygen attacks the CH bond at the α -position to the double C–C bond, which possesses an increased reactivity in oxidation processes. Abstraction of the α -methylene atom H from the compound containing double bonds between carbon atoms leads to the formation of active free radical –CH–CH=CH–, which requires an energy consumption of about 80 kcal/mol. This energy is required in the onset of the reaction for breaking the C–H bonds. The further development of the reaction by the chain mechanism requires a very small amount of energy or no energy at all.

It has been proven experimentally that with the abstraction of the hydrogen atom the double bond is not broken, but that this phenomenon is accompanied by the displacement of double bonds in fatty acid molecules. Herewith, coupled double bonds

$$-C = C - C =$$

appear in the molecules of polyunsaturated fatty acids (containing two or more double bonds), which initially contained only isolated double bonds.

The possibility of the presence of cyclic peroxides

$$\begin{array}{c|c} R_1 - CH - CH - R_2 \\ | & | \\ O - O \end{array}$$

in oxidation products has not been proven to date by direct methods. While hydroperoxides were isolated and studied, cyclic peroxides were not, possibly because of their extreme instability or because they do not exist. In most cases, the proof of the emergence of cyclic peroxides at the advanced stages of oxidation is based on the determination of the general content of peroxide compounds by the iodometric method and the determination of only hydroperoxides by the polarographic method. However, the quantitative differences obtained are within the limits of error of the determination methods.

Hydroperoxides are comparatively unstable compounds easily undergoing various conversions, which lead to the rupture of the O–O bond and the formation of free radicals. The bond rupture energy in peroxides is considerably lower than in the oxygen molecule and makes 30–40 kcal/mol. As the result of dissociation or other conversions of peroxides, the system forms more stable oxidation products as compared with peroxides – the so called secondary oxidation products aldehydes, ketones, low-molecular-mass acids etc. While hydroperoxides have no smell or taste, many of the secondary oxidation products of relatively low molecular masses are involved in the formation of a specific smell and taste of spoiled fats.

The quantum yields determined in photochemical oxidation prove to be much larger

than unity (according to Einstein's law of photochemical equivalence, one quantum of light induces only one chemical reaction), which is a direct proof of the chain nature of the oxidation reactions.

Other proofs of the chain mechanism of the oxidation processes can be the phenomena of initiation (excitation) and retardation (inhibition) of the oxidation reactions. In the former case, oxidation is accelerated in the presence of substances capable of decomposition into free radicals; in the latter, of being inhibited by addition of minor amounts of substances capable of interrupting the chain reaction of oxidation by capturing free radicals that lead the oxidation chain. Oxidation of fats proceeds via formation of free radicals and pertains to the class of slowly evolving chain branched reactions.

Free radicals are highly active particles. Reactions between free radicals and between free radicals and molecules proceed easily; new free radicals are formed in the process to continue the chain reaction.

It is well known that the smaller the activation energy E, the easier the reaction between two reacting chemical compounds is. If two molecular compounds participate in the reaction, the magnitude of the activation energy is usually several tens of kilocalories per mole. In the case of the reaction of free radical with a molecule, the magnitude of the activation energy is not large or equals zero, i.e., E is within the range of 0-10 kcal/mol.

Besides the reaction product (in this case, hydroperoxide), a new free radical (\mathbf{R}^{\bullet}) is formed in the chain reaction mechanism. This radical again enters into the reaction and continues the initiated chain of chemical conversions. Herewith, more new molecules of the initial substance are involved into the oxidation reaction. Thus, the development of the oxidation chain occurs and the involvement of new molecules of the fatty acid or triglyceride.

The chain of oxidative conversions develops until the chain-leading free radicals R^{\bullet} and RO_2^{\bullet} disappear from the system, i.e., as the result of recombination of two radicals. An inactive compound is formed, and the chain terminates. The sooner this happens, the less fatty-acid or triglyceride molecules get oxidized.

Occasionally, the molecular product of the chain reaction in the system where the oxidation process occurs – hydroperoxide – breaks down to form new free radicals, i.e., the chain branches, as each newly formed free radical initiates a new oxidation chain.

The slow development of the oxidation reactions is due to the fact that the branchings of the chain in these reactions are as if "retarded" and occur only at times when hydroperoxides break down to free radicals. These retarded branchings are called "degenerate branchings".

Below, we present a generally accepted scheme of a degenerate branched chain reaction:

 $\begin{array}{ll} RH + O_2 \twoheadrightarrow R' + HO'_2 & \text{Chain initiation (formation of free radical R')} \\ R' + O \twoheadrightarrow RO'_2 & \text{Chain initiation} \\ RO'_2 + RH \twoheadrightarrow RO_2H + R' & \text{Chain continuation} \\ RO_2H \twoheadrightarrow RO' + OH' & \text{Degenerate chain branching} \\ RO'_2 + RO'_2 & \text{R'} + R' & \text{Chain termination} \\ RO'_2 + R' & \text{Chain termination} \\ RO'_2 + R' & \text{Chain termination} \end{array}$

Here RH is the molecule of an oxidizing substance, e.g., a fatty acid; RO_2H is the hydroperoxide molecule; R[•] and $RO_2^{•}$ are free radicals leading the oxidation chain; RO[•] and OH[•] are free radicals formed in the breakdown of the hydroperoxide.



Figure 1.2 A kinetic curve of peroxide accumulation in oxidation of pork rendered suet. Oxidation temperature, 90°C.

The slow development of fat oxidation in the initial stage is due to the delay of chain branching. This stage of oxidation is known under the name of the induction period or initiation period.

However, at later stages of oxidation, when a large amount of free radicals accumulate in the system, the oxidation process is sharply speeded up. The typical autocatalytic character of the kinetic curves for oxidation of fats and related substances is clearly seen by the example of the oxidation of pork rendered fat.

The ability of hydroperoxides to break down to form free radicals, as well as the dependence of the oxidation rate on the extent of oxidation in the cases when hydroperoxides are basically the only reaction products, indicates that degenerate branching in liquid-phase oxidation reactions is due to the breakdown of hydroperoxides in the reaction

ROOH
$$\rightarrow$$
 RO' + OH' or 2ROOH \rightarrow RO' + RO' + H₂O

Below, we will show that oxidation of both melted and solid animal fat proceeds according to the same kinetic law.

The rate of fat autooxidation is commonly characterized, not only in research but also in practice, by the length of induction period, i.e., the length of time during which no pronounced changes in them are observed. This period serves as a preparation to fast oxidation. In the beginning of the induction period, there is no sign of any oxidation products accessible to chemical determination, then peroxides start to be found, and at their sufficient amount, due to the autocatalytic character of the process, oxidation begins to develop at a very high rate, the induction period ends. Upon completion of the induction period, the peroxide accumulation curve sharply rises (see Fig. 1.2).

It should be pointed out that, in an ideal representation, the induction period should be understood to be only that part of the segment of the curve in which peroxides are not found by common chemical (or physicochemical) methods. In practice, in modern production processes, it is difficult to obtain fat not containing peroxides found analytically. In the main, freshly produced fats always contain peroxides in minor amounts. Therefore, for practical purposes a more suitable definition of induction period is that, which is given initially. It is all the more correct as the notion of induction period is conventional, because oxidative changes not registered by chemical methods are observed in fats in the cases when the presence of peroxides is not yet possible to detect by common analytical methods. It is known



Figure 1.3 Kinetic curves of accumulation of fat samples taken at different stages of the technological process (oxidation temperature, 100°C): *1*, after rendering; *2*, from the collector; *3*, from a container.

that hydroperoxides at a concentration of 10^{-6} mol/l can not be found by common chemical methods.

At the same time, the kinetic methods make it possible to register changes in fat at very early stages of oxidation. Studies of fat samples taken from the same commercial batch at different stages of the technological process and containing no peroxides determinable by the iodometric method (peroxides were found in none of the samples) showed that the stability of fat to oxidation as determined by the kinetic method (Fig. 1.3) was different.

Secondary oxidation products include comparatively stable intermediate and end products of oxidation – alcohols, carbonyl compounds, esters, acids, as well as compounds with mixed functions, such as oxy acids, epoxy compounds etc.

It could be said that all secondary products of oxidation emerge as the result of conversions of hydroperoxides; what is more, part of the secondary products are formed immediately at the breakdown of hydroperoxides and the other part, as the result of further reactions.

The primary character of hydroperoxides as the first molecular products of oxidation and the secondary character of carbonyl compounds, alcohols, epoxy compounds and acids is graphically illustrated by curves plotted based on the literature data on the oxidation of methyl oleate under the action of ultraviolet light at 35°C (Fig. 1.4).

The mechanism of formation of secondary oxidation products has been little studied. Only with a small fraction of probability, it could be suggested that ketones are formed from hydroperoxides:

> $R_{1} - CH - R_{2} + R' \rightarrow R_{1} - C' - R_{2} + RH$ OOH $R_{1} - C' - R_{2} \rightarrow R_{1} - C - R_{2} + OH',$ $R_{1} - C' - R_{2} \rightarrow R_{1} - C - R_{2} + OH',$

where R' is either radical 'OH or any of the radicals leading the main chain of oxidation.

It is probable that alcohols are formed from hydroperoxides in degenerate branching of chains



Figure 1.4 Kinetic curves of oxidation of methyl oleate at the action of ultraviolet light: *1*, peroxide oxygen; *2*, carbonyl oxygen; *3*, hydroxyl oxygen; *4*, oxirane oxygen; *5*, carboxyl oxygen.

 $ROOH \rightarrow RO' + OH'$ $RO' + RH \rightarrow ROH + R'$

One of the possible routes of forming epoxy compounds is the intramolecular reaction of the hydroperoxide of the unsaturated compound

According to one of the most probable points of view, acids can be formed from ketones by their oxidation to α -ketohydroperoxide, which subsequently breaks down to form aldehyde and acid

$$\begin{array}{c} R_1 - C - CH_2 - R_2 \rightarrow R_1 - C - CH - R_2 \rightarrow R_1 C - OH + R_2 - C \\ \parallel & \parallel & \parallel \\ O & OOH & O \end{array}$$

It has been proven experimentally that acids are not formed directly from hydroperoxides and emerge as the result of the further conversion of secondary oxidation products, most probably, ketones. As seen from the above reaction, formation of acids proceeds with the rupture of the carbon skeleton of the molecule. Studies of the composition of the acids formed in oxidation of fatty acids and hydrocarbons confirm this, because in practice only acids with a shorter carbon chain than in the initial compound could be isolated from the oxidizing mixture.

The described mechanisms of formation of secondary oxidation products are basically hypothetical and were proposed mainly based on the studies of hydrocarbons of the olefin and paraffin series. However, they can be accepted with an equal degree of probability for oxidation of fatty acids.

This can be done based on that in such acids being part of fats as, e.g., oleic, linolic or linolenic acids, oxidation at the initial stages affects carbon atoms removed from the ester group by a chain of at least six methylene groups. Therefore, the ester group can have no influence on the oxidation process, and oxidation proceeds the way it does in the respective unsaturated hydrocarbon.



Figure 1.5 Dependence of the rate of oxidation of fatty acids in the air at a temperature of 37° C on the number of double bonds in them: *1*, ethyl oleate; *2*, ethyl linoleate; *3*, ethyl linolenate; *4*, methyl arachidonate.



Figure 1.6 Kinetic curves of oxidation of pork suet at different temperatures: *1*, 90°C; *2*, 100°C; *3*, 110°C; *4*, 120°C.

Products of oxidation of fats and oils, as well as fatty acids and their derivatives are found to have oxidation products belonging to the same groups of organic compounds, which were found in hydrocarbons of the olefin and paraffin series, i.e., alcohols, carbonyl compounds, epoxy compounds, acids etc.

For instance, carboxyl compounds of oxidized fats identified by chromatographic, spectrophotometric and other methods include *n*-hexanal, 2,4-decadienal, propionic aldehyde, 2-hexanon, 2-octanon, 2-nonanon, 2-decanon, *n*-pentenal, acetaldehyde etc.

The reactivity of fatty acids increases with the increase of the number of double bonds in the molecule. Figure 1.5 shows a dependence of the oxidation rate of unsaturated fatty acid esters on the number of double bonds.

Formation of free radicals in the system is facilitated with the temperature increase. Herewith, the chain initiating rate and, therefore, the oxidation rate, increases. Kinetic curves of pork fat oxidation illustrating this are presented in Fig. 1.6.

If chain initiation occurs mainly according to the reaction $RH + O_2$, then the rate of



Figure 1.7 Effect of oxygen pressure on the rate of oxidation of ethyl linoleate at 45°C.

initiation should depend on oxygen pressure. The occurrence of this dependence at small conversion rates has been established in oxidation of ethyl linoleate. From Fig. 1.7, it follows that the rate of ethyl linoleate oxidation on oxygen pressure becomes pronounced at a pressure less than 200 mm Hg. However, it should be noted that the pressure range in which a pronounced dependence of the oxidation rate on oxygen partial pressure is still pronounced can change within broad limits in transition from one compound to another.

Processes of oxidative spoilage of fats, as well as other chain reactions, are also affected by light and ionizing radiation, which contribute to the emergence of free radicals in the system.

The action of light of certain wavelengths and especially UV light on fats increases the rate of emergence of free radicals, which leads to a fast oxidative spoilage of fats.

In the use of ionizing radiations to increase the stability of meat and meat or other food products in storage, the most serious negative consequence of irradiation is oxidation of fats. The emergence of free radicals in the presence of oxygen leads to the formation of peroxide radicals RO_2^{\bullet} and, therefore, peroxides and products of their conversion.

Variable valence metals – iron, copper and others, which get into fats from the equipment in their processing, are efficient catalysts of oxidation processes.

The catalytic acceleration of the oxidation reactions by these metals is based on that, depending on the valent state, they can either attach an electron or donate it to any valent saturated particle, which leads to the activation of radical breakdown of hydroperoxides according to the following mechanism:

$$ROOH + Fe^{2+} \rightarrow Fe^{3+} + RO' + OH^{-}$$
$$ROOH + Fe^{3+} \rightarrow Fe^{2+} + ROO' + OH^{+}$$

Iron is not consumed in this process and, therefore, being present as traces, it contributes to the emergence of radicals RO[•] and RO₂[•], which initiate the chain process of oxidation. By the example of metal-catalyzed oxidation of methyl linoleate, it has been shown that metals accelerate the oxidation process only in the presence of the peroxides of oxidized material or of specially added peroxides.

From literature data, it follows that lead has the largest catalytic efficiency, which is followed by copper, iron, tin, zinc and, finally stainless steel.

Traces of metals contribute to spoilage of animal fats, which is called tallowiness. In practice, tallowiness is observed, e.g., in excessive intensive mechanical treatment of fats,

owing to a lengthy contact with metal apparatuses or long-time storage of fat in a metal container. Tallowiness occurs without a significant accumulation of peroxides. The main oxidation products in this case are oxy acids and, possibly, polymerization products.

The catalytic activity of variable-valence metals increases considerably if they enter into the reaction with some specific organic compounds, especially proteins.

Meat and blood pigments myoglobin and hemoglobin, as well as their derivatives are strong catalysts of oxidation of lipids of meat, meat products, fatback.

This, in particular, is confirmed by the acceleration of linoleate oxidation in the presence of extracts of hog muscle tissue. Coagulation of proteins considerably decreases the catalytic activity of meat pigments. Hemoglobins of different animals differ insignificantly by their catalytic action on the process of linoleate oxidation.

A decrease of temperature contributes only moderately to the decrease of the rate of oxidation catalyzed by meat and blood pigments.

Fresh meat pigments, as well as their derivatives are nonspecific catalysts, e.g., hematin also contributes well to oxidation of hydrocarbons and also fatty acids.

Though fat oxidation catalyzed by heme compounds has been known since long, the mechanism and chemistry of this process have not been made clear until now, possibly owing to the exceptional complexity of this phenomenon.

There is no doubt that both forms of iron (Fe^{2+} and Fe^{3+}), which are components of heme compounds, initiate the breakdown of hydroperoxides and, thus, accelerate oxidation of fat. But there is also no convincing proof that the Fe^{3+} -containing pigment is capable of accelerating oxidation of lipids in the absence of hydroperoxides, though, according to the literature data, this is believed to be possible.

The presence of oxidation products in fats is revealed, as well as the extent of the oxidation process is assessed by using chemical, spectrophotometric, chromatographic, polarographic etc. methods.

Methods of determining compounds of peroxide character have become widespread. Especially frequently, the iodometric method of determining peroxides is used. The iron–rhodanide, indophenol, iron–chloride–indophenol, polarographic, stannochloride etc. methods are used more rarely.

The content of peroxides in edible fats and oils, as well as in food products is expressed in different way. In the Russian Federation, it is accepted to express the content of peroxides in percent iodine; in the UK, in millilitres of a 0.002 N solution of thiosulfate per gram of fat (Lee number). In the USA, the peroxide content is expressed predominantly in milliequivalents or millomoles of active oxygen of peroxides per 1000 g of fat.

There is a certain dependence between the magnitude of the peroxide number and the organoleptic rating of the quality of fats and fat-containing products, because peroxides in them accumulate in parallel with the emergence and development of rancid smell and taste.

In fatty tissue separated from a freshly killed animal, it is impossible to find fatty peroxides, because they are not a normal metabolic product in the animal organism. However, fatty peroxides can be formed in the organism of the alive animal in pathological cases, e.g., under the action of ionizing radiation.

As we pointed out, peroxides emerge in fat during the technological treatment and storage. Delays of the raw materials before rendering, high temperature, the presence of atmospheric oxygen, the contact with metal equipment, long-time treatment, effect of light, incorrect condition of storing the final product – all these contribute to the emergence and further accumulation of peroxides in fat.

The relation between the organoleptic evaluation of the extent of fat spoilage and the