CHEMISTRY & CHEMICAL TECHNOLOGY

*Chem. Chem. Technol., 2024,*
*Vol. 18, No. 2, pp. 284–294*

**Chemical Technology**

# THE PROBLEM OF ROAD BITUMEN TECHNOLOGICAL AGING AND WAYS TO SOLVE IT: A REVIEW

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https://doi.org/10.23939/chcht18.02.284

**Abstract.** This paper discusses the main features of technological aging of bitumen, in particular, the mechanisms and transformations that accompany this process. The main laboratory methods for modeling the above processes are considered. It is described how the technical essence of the methods has changed from the first developments to the present. A number of compounds that can be used as inhibitors of technological aging, including antioxidants and plasticizers, as well as some "natural" substances that have these properties, are presented.

**Keywords:** bitumen modification; technological aging; short-term aging; aging resistance.

## 1. Introduction

In recent decades, the development of the road construction industry both in Ukraine and worldwide has been gaining wider scope and growth rates. The main reason for this is the unprecedented increase in the number of vehicles. According to the literature[1], by 2040, the world vehicle fleet will increase by 80 % to two billion cars.

In this regard, the construction of roads that meet all the requirements for comfort, speed, and efficiency of passenger and cargo transportation, as well as the most important indicator − traffic safety − is a top priority. At the same time, asphalt concrete pavements have become the most popular, as they meet all the requirements for the roadway. Asphalt concrete pavement can be subjected to high loads immediately after laying. Another advantage of such roads is that the tires of vehicles do not slip on them, as the asphalt concrete provides excellent grip. Road markings are easy to apply and hold perfectly on this type of road surface. Such pavements are easy to wash and clean. In addition, asphalt concrete pavements serve for decades and are relatively easy to repair[2,3].

At the same time, given that an asphalt concrete mixture is a complex multicomponent material, it changes its properties depending on the change in the composition of the components. A binder, *i. e.*, bitumen, is responsible for maintaining the main operational characteristics of this mixture. Considering the wide range of applications of bituminous materials – as roofing materials (roofing bitumen, roofing felt, glassine); for waterproofing (insulating bitumen); as mastics and pastes for protecting pipelines or gluing building materials – their essential drawback is that these binders lose their properties during their manufacture, storage, and technological processing, that is, they are subject to technological aging[4].

Moreover, the rate at which the binding properties of bitumen deteriorate depends primarily on the quality of the source material. Therefore, various additives and modifiers are added to bitumen in order to increase the service life of road pavement.

Two types of aging are known. Technological aging occurs at the stage of manufacturing bitumen and asphalt concrete road pavement and laying the latter in the roadbed. Operational aging occurs under the impact of environmental factors and mechanical loads from vehicle wheels on the roadbed. This article provides an overview of both the main factors that lead to the technological aging of bitumen and the mechanisms accompanying the process. Comparative characteristics of the methods that simulate the process of technological aging of bitumen in the laboratory are also given, and several modifiers that can be used as inhibitors of this process are considered.

## 2. The Main Features of Technological Aging of Bitumen

It is well-known that bitumen is affected by many technological factors from the binder production stage to its use in the roadbed. These factors cause the internal transformations and changes in the structure of bitumen. The processes occurring there include the following: oxidation, evaporation of components with the lowest

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molecular weight (*i. e.*, the most volatile ones), and physical (steric) hardening. Oxidation has the greatest impact on the deterioration of bitumen properties. Oxidative aging belongs to irreversible diffusion phenomena, which are mainly controlled by thermal reactions between the atmospheric oxygen and the bitumen components. This leads to changes in its chemical properties. This process is also influenced by photooxidation reactions which facilitate further exposure to oxygen[5–9].

In numerous studies of the chemical composition, structure, and properties of high molecular weight compounds of oil, it has been considered that oxidation associated transformations primarily result in the formation of asphaltenes from resins and their further transformation into carbenes and carboides[10]. Changes in the group composition of bitumen during aging have been also examined in a series of papers. Oils have been found to convert to resins, and those, in turn, convert to asphaltenes. Furthermore, the conversion of oils to resins is much slower than the conversion of resins to asphaltenes, resulting in a significant increase in the quantity of asphaltenes in bitumen for a certain period of time. At the same time, the quantity of resins that provide plasticity and stretchability decreases. With increasing the content of asphaltenes, the plasticity of bitumen deteriorates while its brittleness increases, which negatively affects the binding properties.

As compared with the oxidation process, the contribution of volatile evaporation during aging is limited[11,12]. This conclusion can be explained by the fact that the content of volatiles in bitumen is not too high, because they are used in other branches of oil refining as a valuable component. On the other hand, the volatile content in bitumen is low due to the restrictions on potentially toxic smoke emissions when bitumen is heated.

Evaporation of volatiles (both saturated and aromatic hydrocarbons) depends mostly on temperature since the main part of volatiles evaporates during mixing and laying asphalt concrete mixture.

Oxidation and evaporation, which are irreversible processes, proceed rather slowly at room temperature, while their effect is accelerated when the bitumen is exposed to high temperatures during preparation, transportation, or laying of the mixture. In general, temperature has a significant effect on the aging rate. Thus, the oxidation rate doubles with each increase in temperature by 10 °C above 100 °C[13,14].

In terms of chemistry, bitumen aging is "automatic" oxidation, as the binder reacts with oxygen to produce new compounds that also react with oxygen, thus continuing the aging. It can be argued that the components pass from more non-polar fractions to more polar ones, as oxygen-containing functional groups are formed in bitumen[15].

Unlike the previous processes, physical (steric) hardening is reversible, that is, it changes the rheological properties of bitumen without changing its chemical composition[16]. This mechanism is related to the formation of ordered structures by paraffins in the maltene phase, which is affected by linear alkanes present in the asphaltene fraction. The physical hardening also proceeds quite slowly at room temperature, while it speeds up at low temperatures due to the internal rearrangement of the binder molecules. The effect of this process is quite moderate and consists of the binder hardening, which disappears upon heating without affecting the final characteristics of bitumen[5,14].

There are quite contradictory opinions on the impact of the initial bitumen composition on aging. Considering the bitumen aging as a complex process that proceeds with the formation of free radicals which react with each other to form a network of high molecular compounds, Mertens[17] proved that the presence of a large quantity of asphaltenes in the initial bitumen leads to the system heterogeneity and syneresis with the release of oils upon oxidation. On the other hand, a significant content of asphaltenes improves the bitumen stability, and maximum stability is observed at an asphaltene content of about 22 %[18].

In studies on the bitumen aging mechanism, the positive impact of aromatic hydrocarbons, which peptize asphaltenes, has been proven. Moreover, outside Ukraine, bitumen is mainly obtained from crude oil by low-temperature vacuum distillation methods, which ensures a high quality of bitumen. In Ukraine, the most common technology for bitumen is based on oxidative dehydrogenation. In this event, the raw materials are oil processing wastes and tar. The bitumen obtained in this way is of somewhat lower quality with worse homogeneity and binding properties[19].

In terms of its properties, distillation bitumen has several advantages over oxidized bitumen, *i. e.*, it possesses a higher plasticity and good adhesive properties, facilitates the hydrophobicity of asphalt concrete, and increases the service life of road pavement. Since oxidized bitumen does not have such a plasticity interval and exhibits worse ductility compared to distilled bitumen, there is a need to add various admixtures to the binder formulation. Hence, the comparison of production technologies and the analysis of the properties of bitumen obtained in different ways prompts an in-depth study of approaches to solve the issue of their technological aging[20,21].

Studying technological aging, it appears that the weakest link of asphalt concrete plants, which greatly impacts bitumen degradation, is the storage where bitumen is kept. There are numerous disadvantages of pit-type storage, which are most widely used compared to other ground-type storages. Usually, underground storage is the reservoirs made of reinforced concrete, which have inclined or vertical side walls and consist of one or several storage compartments. On the one hand, less effort is required to fill such storage. On the other hand, in the case of poor waterproofing, the water saturation of bitumen is observed and this undoubtedly requires costs for its further dehydration. In addition, there is a "mirror" of contact with air in underground storages, and pumping is carried out by a jet in an open chute, intensifying a binder oxidation. The advantages of ground storage become obvious, although the technology of their applications is not perfect either, since one of the issues in solving the problem of technological aging of bitumen is the features and details of its production technology[22].

Besides, some technological operations, particularly mixing components in a mixer or laying an asphalt concrete mixture, have a significant effect on the properties of asphalt concrete and lead to the appearance of microdefects. The latter ultimately affects the durability of the road pavement. While preparing the asphalt concrete mixture, the selection of the mineral part is also important considering that the chemical and mineralogical composition of the ingredients and the granulometry type significantly contribute to the structure and texture of the asphalt concrete.

Since already at the first technological stage, the aging index of bitumen is five times higher in comparison with that at the operational stage, slowing down the rate of loss of bitumen binding properties at this stage should significantly extend the service life of the final asphalt concrete pavement[23–25].

## 3. Inhibitors of Bitumen Aging

Some polymers, waxes, heavy pyrolysis resin, adhesive additives (mostly cationic surfactants), or complex modifiers can be mentioned among the compounds that can extend the binder service life and, accordingly, slow down the technological aging. At the same time, the slowing down of aging for these bitumen modifiers is often only an additional positive effect, while these modifiers are not directly used in industry as aging inhibitors. To this end, a number of different compounds are used, such as antioxidants or plasticizers.

The plasticizers reduce the viscosity of the dispersion medium (oil and resins) and the number of structural elements (asphaltenes) per unit of bitumen volume. Taking into account that plasticizers are mainly designed to "dilute" the binder, they include tar, oil fuel, oil extracts, industrial oils, *etc.*[4].

Antioxidants are used to slow down or block oxidation reactions that occur while heating the binder and contacting with the oxygen of the air. Depending on the antioxidant action mode they are divided into primary antioxidants capable of "scaring off" radicals and secondary antioxidants which are designed to inhibit the formation of peroxides, thereby preventing the beginning of the oxidation process. Primary antioxidants include vitamin E, furfural, butylated hydroxytoluene, "protective" phenolic antioxidants, and stabilizers. The secondary ones are dilauryl thiodipropionate (DLTDP), aminogenic surfactants, N-phenyl-2-naphthylamine, zinc dibutyldithiocarbamate (ZDBC), thin-crystalline aliphatic hydrocarbons with long chains, polyfunctional additives based on fatty amine surfactants and polyethylene, $C_{18}$ fatty unsaturated acids, derivatives of fatty amines, *etc.*[26–33]. Ouyang *et al.*[31], as well as Martin[34], considered primary antioxidants to be more effective, but it is also possible to combine primary and secondary antioxidants into complexes, which in some cases allows to ensure their higher thermo-oxidative resistance[27].

At the same time, four main groups of compounds capable of slowing down the oxidation of hydrocarbons in bitumen are identified[35]:

– phenols that break the chain reaction with peroxyl radicals;

– inhibitors that slow down aging by reacting with alkyl radicals;

– agents that break peroxides without the formation of free radicals;

– agents that consume oxygen molecules faster than they enter into oxidation reactions.

Among the compositions that include these additives, the most widely used are amines, "preventing" phenols (with one or more bulky functional groups, *e. g.*, tret-butyl), phosphites, and organic zinc compounds[27,31]. However, the use of organic zinc compounds requires significant economic costs, which is a serious obstacle to their widespread use[36].

To improve the aging resistance of bitumen binders, many nanomaterials have been successfully applied[37,38]. Nanomaterials are materials with at least one of their dimensions less than 100 nm, and the small particle size endows them with novel properties and functions.[39] Previous studies have demonstrated that by incorporating nanoparticles as a modifier into bitumen, its resistance to aging can be increased[40,41]. Fini *et al.*[42] added different concentrations of nano-silica (nano-$SiO_2$) in the base bitumen to examine its effects on rheological performance and oxidative aging. Further, the results demonstrated that nano-$SiO_2$ (NS) improves the rheological properties and oxidative aging resistance of bitumen binder. Also, it has been demonstrated that the fatigue life and rutting resistance of bitumen can be increased by adding nanofillers[43,44]. For instance, nano-$Fe_2O_3$ can significantly improve the stiffness and deformation resistance of bitumen[45], whereas nano-$TiO_2$ can improve its fatigue properties[46]. All these improvements in the properties of bitumen can be directly or indirectly attributed to the nanoscale size of the particles[47].

Nanomaterials possess a significant surface charge, leading to their tendency to aggregate when incorporated into bitumen modifications[48]. Such agglomeration can impede or even compromise the desired modification effects of nanomaterials. To address this issue, surface modification techniques are commonly employed[49]. By employing these techniques, the compatibility between modified nanomaterials and bitumen can be enhanced, thereby restraining the agglomeration of nanoparticles within the bitumen matrix and facilitating the effective utilization of nanomaterials for modification purposes[50]. Mousavi and Fini[51] utilized the surface functionalization of silica nanoparticles (SiNPs) with various coupling agents to improve their compatibility and miscibility in the organic medium of bitumen. The results showed that the dual functionality of silane coupling agents allowed them to connect SiNPs with bitumen components. Although surface modification can mitigate agglomeration, the production of nano-modified bitumen has become more complicated and results in increased costs. Conventional nanomaterials are typically characterized by their expensive production processes. Consequently, the high cost associated with the modification of nanomodified bitumen has hindered its widespread application in conventional bitumen pavements[52]. However, an alternative nanomaterial known as fumed silica nanomaterials (FSNs) has emerged, which exhibits distinctive nanoscale properties despite its relatively larger particle size. The larger particle size of FSNs reduces their production cost to 10 % of that of NS particles, facilitating their wide applications in anti-aging rubber applications[53]. Due to the use of nanoparticle chain aggregates as a basic unit[54,55], fumed silica can be employed as fillers to improve the rheological properties of resins and coatings. To recapitulate, previous studies have demonstrated that NS plays a crucial role in increasing the bitumen's resistance to aging. However, NS particles are susceptible to agglomeration in the bitumen matrix due to their small size and high surface energy. In addition, the high modification cost limits the use of nano-$SiO_2$ as a modifier for bitumen[56].

Another area of research that is gaining popularity is the use of simple and natural substances as anti-aging agents, which can also be found directly in the environment. Thus, in recent years, the attention of researchers has increased significantly to such "natural" antioxidants as phospholipids, ascorbic acid, diatomaceous earth, lignin from rice husks and wood, *etc.*

The results show that lignin-modified bitumen had better aging resistance than virgin bitumen. Meanwhile, the changes of functional groups in the infrared spectra proved that the thermal-oxidative aging mechanism was the decomposition of lignin itself under the action of thermal oxygen, which inhibited the aging process of bitumen[57]. However, some researchers have concluded that the effect of lignin on the low-temperature properties of bitumen was not significant. The molecular weight and functional groups of lignin can be adjusted by different biological and chemical processes, which can lead to significant improvements in its low-temperature properties[58–60].

In line with these trends, chitosan and its derivatives can also be used as inhibitors of the bitumen short-term aging[61]. Chitosan is one of the main chitin derivatives[62] belonging to mucopolysaccharide found in the exoskeletons of crustaceans, insects and fungal cell walls. The currently available data indicate that 100 trillion tons of chitin is produced annually[63,64]. Structurally, it is a derivative of cellulose with amino groups instead of hydroxyl groups and consists of β-glucosamine molecules linked by β-1,4-glycosidic bonds[65]. The extraction process of chitin from the biological source includes three main steps: (I) deproteinization of the material with an alkaline solution, (II) demineralization with an acid solution, and (III) decolorization with an alkaline solution[64,66,67]. The chitin obtained in this way is a substrate for the production of chitosan, which is a natural, non-toxic polymer insoluble in water and many organic solvents and used in many fields of science and industry[68].

To reduce the effect of short-term bitumen aging, two-component polymer composites based on chitosan-containing ligands with different chemical structures, *i. e.* polyaniline, methacrylamide and 2-acrylamido-2-methylpropanesulfonic acid were investigated. The studies showed that amine-rich chitosan:polyaniline polymer composite is the most promising. Its application enables to reduce the hardening and increases the softening temperature, as well as dynamic viscosity during short-term aging. Moreover, the chitosan:polyaniline composite reduces oxidation and aromatization reactions of bitumen components[61].

Humic substances also belong to natural components[69–73]. A range of humic substances include humic and hymatomelanic acids, fulvic acids, and humin. Among them, humic acids themselves or their salts, in particular, potassium humate, are of the greatest value. Depending on the raw material, this salt can be extracted from peat, lignite, or leonardite by using a dilute alkaline solution. In addition, the content of humic acids in the final product will also vary depending on the raw material type. For instance, the acid content in lignite is the lowest and accounts for up to 25 wt. %, in peat – from 20 to 70 wt. % by weight, and, in leonardite, the content of humic acids is the highest and can reach 95 wt. %.

Thus, it can be concluded that none of the above-mentioned methods is perfect and without drawbacks. Nevertheless, researchers have managed to achieve maximum plausibility when using laboratory methods for modeling the technological aging of bitumen in comparison with real conditions. Hence, the most widely used methods today are TFOT and RTFOT, which are included in the standards of many countries.

Moreover, it was found that, with an increase in the content of humic acids starting from the introduction of potassium humate obtained from peat (30 wt. % of humic acids) and with a further increase in the acid concentration for potassium humate from leonardite (85 wt. % of humic acids), their effect on slowing down the aging is more pronounced. The optimal amount of the modifier in this case is 1–3 wt. %[74–85].

## 4. Laboratory Methods of Modeling Technological Aging

To study the transformations that occur in bitumen during technological aging and to estimate the efficiency of aging inhibitors, special techniques have been developed. These techniques allow reproduction of binder technological aging in the laboratory.

Among other methods, the above-mentioned ones can be categorized as static, in which a bituminous binder is in a stationary state, and dynamic, in which a bitumen film is either scrolled or mixed.

Comparative characteristics of the main indicators of these methods are given in the Table.

Thus, one of the first methods for modeling technological aging was developed in the USSR according to GOST 11954-66, which was borrowed from GOST 2400-51. According to the method, bitumen is poured into a metal or glass cup with a layer thickness of about 1 mm and then placed in a thermostat, where it is heated to a temperature of 160±0.5 °C and kept it at this temperature for 5 hours. Further tests are carried out upon cooling the bitumen to a temperature of 25 °C. The resistance to hardening is estimated by the change in the penetration depth of a needle at 25 °C. The softening temperature upon heating is not normalized; it is measured just for data accumulation. This GOST 11954-66 method was replaced with GOST 18180-72. Until recently, this method was used to determine the changes occurring in bitumen during heating due to volatile evaporation. The method was used mostly to determine the bitumen stability during the long-term storage at elevated temperatures by calculating by changes in the binder softening temperature before and after heating.

**Table.** Methods of Modeling Technological Aging

| Test method | Value | | |
|---|---|---|---|
| | Film thickness, mm | Temperature, K | Duration, h |
| GOST 11954-66 | 1 | 160 | 5 |
| GOST 18180-72 | 4 | 163 | 5 |
| TFOT | 3.2 | 163 | 5 |
| MTFOT | $100 \cdot 10^{-3}$ | 163 | 24 |
| Shell Microfilm Test | $5 \cdot 10^{-3}$ | 107 | 2 |
| F. Hveem method | $20 \cdot 10^{-3}$ | 99 | 24 |
| RTFOT | 1.25 | 163 | 1.15 |
| RTFOTM* | 1.25 | 163 | 1.15 |
| RMFOT | $20 \cdot 10^{-3}$ | 99 | 48 |
| TFAAT | $160 \cdot 10^{-3}$ | 113 | 72 |

* In this method, metal rods are additionally used.

The main differences between the methods for aging modeling according to GOST 11954-66 and GOST 18180-72 are different aging temperatures (160 and 163 °C, respectively), as well as the thickness of a bitumen film, is subjected to aging. Thus, according to the former method, the film thickness is 1 mm, while the latter one is 4 mm.

Unfortunately, the technical essence of the method has not changed since 1939. Only one parameter used to evaluate aging has changed, namely, the needle penetration depth at 25 °C has been replaced by the softening temperature. In addition, a sample film thickness underwent significant changes (increased by 4 times), which actually reduced the accuracy of the experiment.

Conducted outside Ukraine studies of bitumen aging in the laboratory turned out to be more progressive and informative.

Thus, over the past 70 years, foreign researchers have made numerous attempts to compare laboratory aging methods so that they correspond to the processes occurring in bitumen under real conditions during production, storage, and laying. There have been even separate experiments with ultraviolet and microwave interactions, although most of the research has been aimed at studying the changes occurring in thin bitumen films upon heating in an oven.

One such method is the Thin Film Oven Test (TFOT) proposed by R.H. Lewis and J.Y. Welborn in 1940. The method was developed to distinguish bitumens by: (i) their ability to lose volatile components and (ii) the change in resistance to hardening. In this method, a bitumen sample with a volume of 50 mL is used. The sample is placed into a flat metal container with a diameter of 140 mm. Here, the bitumen layer thickness is 3.2 mm. At least two such containers are placed in an oven on a shelf rotating with a speed of 5 to 6 rpm at a temperature of 163°C for 5 hours[19,86].

The TFOT method was adopted by the American Association of State Highway Officials (AASHO) in 1959, and then, in 1969, by the American Society for Testing and Materials (ASTM) as a method for estimating bitumen aging during manufacturing asphalt concrete mixtures at asphalt concrete plants (ASTM D1754-94)[87]. The main criticism of this method is that only the upper layer of bitumen is affected during aging, and the lower layers are not subject to oxidation, as they are protected by the upper layer. Since the bitumen is not mixed, there is a risk that aging, *i. e.*, volatile loss, is limited to the "film" of the bitumen sample. The concern that the TFOT method for relatively thick films is not efficient enough has prompted researchers to develop new aging methods by reducing bitumen film thickness. The Modified Thin Film Oven Test (MTFOT) became one of the options. In this technique, the binder film was reduced to 100 μm with an additional increase in the aging time to 24 hours. This modification of the TFOT method allowed both intensifying the aging process and including hardening of the binder due to its oxidation.

Another modification of the TFOT method is the Shell Microfilm Test. In this trial, a very thin bitumen film (5 μm) is kept on a glass plate at a temperature of 107 °C for 2 h. This film thickness was chosen based on the thickness of a bitumen film that forms on the stone material surface in the asphalt concrete mixture. Bitumen properties are estimated by comparing viscosity before and after aging to determine the aging index. However, the relationship between aging in real conditions and laboratory aging has not been confirmed by this method except in the work conducted by the Zaka-Wigmore Test company in 1969[21].

The Shell Microfilm Test was modified by F. Hveem *et al.* in 1963[88]. A bitumen film thickness was enlarged to 20 μm, and the aging time was increased to 24 hours. At the same time, the test temperature was reduced to 99 °C. The changes exhibited an indirect relationship between aging in real conditions and the laboratory. Chronologically, the next aging method is the Rolling Thin Film Oven Test (RTFOT), the most significant modification of the TFOT method. The RTFOT method was developed by the California Division of Highways. According to this method, a bitumen sample is placed in a glass flask, which is rotated during aging and thus keeps bitumen in thinner films compared to TFOT. The average film thickness does not exceed 1.25 mm. Aging occurs with a constant supply of air at 163 °C for 75 minutes. The RTFOT method allows heat and air impact on the entire bitumen sample whereas continuous mixing ensures that it occurs in real ones. Nevertheless, experience has proven that the aging carried out according to this technique correlates quite well with what is observed in the mixing process in plants. The RTFOT method was approved as a standard by ASTM under the standard ASTM D2872-19 in 1970[89].

Remarkably, as was confirmed by several works, the RTFOT and TFOT methods are not interchangeable, since the change in properties by the RTFOT method is more pronounced than by the TFOT method for most bitumens. This is primarily due to the different film thickness (1.25 mm for RTFOT *vs.* 3.2 mm for TFOT)[5,19].

The RTFOT method is believed to better mimic the change in bitumen properties that occur during the preparation of asphalt concrete mixtures compared with the earlier methods. Nevertheless, this method has some drawbacks as well. One such disadvantage is the impact of the high viscosity of modified bitumen on the rotation of the binder in flasks during aging. Some modified bituminous binders are even capable of leaking out from the flasks during testing.

Nowadays, the RTFOT method is one of the main methods of the Superior Performing Asphalt Pavements (Superpave) system, developed in the USA. The essence of this system lies in a new categorization of binders and fundamentally different methods of testing bitumen and asphalt concrete pavements. Another important feature of the system is designing optimal formulations to ensure the operational durability of the road pavements laid on specific sites under known climatic conditions[90].

However, despite the worldwide recognition of the Superpave system, it is not used everywhere. In most European countries and China, widely used equipment and methods for testing road materials are similar, but the Superpave system has not been fully implemented.

To avoid the problems that may arise when using the RTFOT method for modified bitumens, H. Bahia *et al.*[91] suggested the Modified Rolling Thin Film Oven Test (RTFOTM) method in 1998. This method is identical to the RTFOT method, except that steel rods with a diameter of 6.4 mm and a length of 127 mm are installed in the glass flasks during trials. The rods help to forcefully distribute a high-viscosity bituminous binder. Initial experiments by H. Bahia proved that the use of steel rods has little effect on the bituminous binder's physical properties, which were determined by the penetration values. Recent studies at the Turner-Fairbanks Highway Research Center (TFHRC) have revealed that the application of steel rods does not solve the problem of uniform distribution of a modified bitumen binder. Further research is needed before this method can be used.

The Rolling Microfilm Oven Test (RMFOT) is another method that originated as a modification of the RTFOT method. The RMFOT method was developed to prepare thinner bitumen films for technological aging. The essence of the method is the bitumen dissolving in gasoline followed by the solution distribution over the inner surface of an RTFOT flask. Afterward, the gasoline undergoes evaporation to form a 20 μm uniform film on the flask walls. A sample prepared in such a way is kept at a temperature of 99 °C for 24 hours. A significant drawback of this method is a rather small amount of the aged material obtained in an RTFOT flask (about 0.5 g) which may not be enough for further examination.

Developed by Petersen in 1989, the Thin Film Accelerated Aging Test (TFAAT) is a modification of the RMFOT method. Compared to the RMFOT method, TFAAT has its advantages. A sample weight is enlarged to 4 g in TFAAT compared to 0.5 g in the RMFOT method. Another option for improving the RTFOT method is the increase in the temperature to 113 °C[19]. The temperature choice is not accidental; it is obtained by comparison of the modified method, which was performed using a rod, and the standard RTFOT method. As a consequence, both tests showed the same results at the chosen temperature. Hence, it was concluded that the use of a metal rod was no longer needed when this temperature was reached. One of the latest innovations is the Nitrogen Rolling Thin Film Oven Test (NRTFOT) developed in 2000. The test consists of testing a binder in thin films in an inert environment[92].

In addition to that, some techniques significantly differ in the method of aging samples. Thus, the China University of Petroleum proposed a dynamic model of the first order, which is based on the maximum amount of oxygen that bitumen can absorb. The aging dynamics of asphalt concrete was also studied using IR spectroscopy and gas chromatography. Aging was also explored by changes in kinematic viscosity at 60 °C[5].

It should also be noted that almost all of the above-mentioned foreign aging methods are aimed at imitating the processes that occur during the production and laying asphalt concrete mixtures, *i. e.*, technological aging. Thus, further study of operational aging was carried out on binders aged at the first stage.

## 5. Conclusions

Given that the development of the road construction industry both in Ukraine and worldwide has been gaining wider scope and growth rates, high-quality road pavements that meet all the regulation requirements and the main criterion – traffic safety – are of great importance. Nowadays, the pavements having the required characteristics are asphalt concrete ones – complex multicomponent mixtures able to change their properties depending on the change in the component composition.

The main ingredient that forms the structure of any asphalt concrete mixture and determines its main operational characteristics is a binder, *i. e.*, bitumen. However, the main disadvantage of bituminous binders is that they lose their properties during manufacture, storage, and technological processing, that is, they are subject to technological aging. The main processes occurring thereat include the following: oxidation, evaporation of components with the lowest molecular weight (*i. e.*, the most volatile ones), and physical (steric) hardening. Bitumen was also found to change its group composition during aging, in particular, oils convert to resins, and those, in turn, convert to asphaltenes. In addition, the conversion of oils to resins is much slower than the conversion of resins to asphaltenes, resulting in a significant increase in the quantity of asphaltenes in bitumen for a certain time. At the same time, the quantity of resins that provide plasticity and stretchability decreases. With the increasing content of asphaltenes, the plasticity of bitumen deteriorates while its brittleness increases, which negatively affects the binding properties.

Given the technological aspects of asphalt pavement production, the main loss of bitumen properties is observed when pumped by jet in an open chute into a storage facility, as well as when mixing bitumen with stone materials at elevated temperatures and subsequent laying of the final pavement.

In this case, adding inhibitors and modifiers to bitumen is needed. They allow preserving bitumen binding properties at a high level for a long time. To this end, antioxidants, plasticizers, or nanomaterials are used.

In particular, tar, oil fuel, oil extracts, and industrial oils are used as plasticizers, while antioxidants, depending on the mode of action, are divided into primary (vitamin E, furfural, butylated hydroxytoluene, "protective" phenolic antioxidants, and stabilizers) and secondary, which include: DLTDP, aminogenic surfactants, ZDBC, thin-crystalline aliphatic hydrocarbons with long chains, polyfunctional additives based on fatty amine surfactants and polyethylene, $C_{18}$ fatty unsaturated acids, and derivatives of fatty amines. It is also possible to use antioxidant complexes that combine primary and secondary antioxidants. Among the compositions capable of slowing down technological aging processes, the most widely used today are amines, "preventing" phenols with one or more bulky functional groups (*e. g.*, *tert*-butyl), phosphites, and organic zinc compounds. However, taking into account their high cost and difficult availability, the issue of technological aging inhibitors is still a challenge. An alternative in solving this issue can be bitumen modification with complex modifiers, the applications of inexpensive and efficient modifiers from various wastes or "natural" substances like humic acids and their salts.

Another important issue concerns the method that should be used to test a binder for its resistance to technological aging. Currently, numerous methods are worldwide known for estimating binder aging. They allow mimicking of the processes that occur during the production and laying of binders. However, each of the described methods has its advantages and disadvantages, which can significantly affect the reliability of the final results. At the moment, the most widely used methods for modeling technological aging are TFOT and RTFOT, which are included in the Superpave system and are standardized in many national standards in Europe and the United States. At the same time, newer and more technologically advanced methods may likely replace them, as research in this area is still ongoing.

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*Received: January 09, 2024 / Revised: February 07, 2024 / Accepted: March 11, 2024*

# ПРОБЛЕМА ТЕХНОЛОГІЧНОГО СТАРІННЯ ДОРОЖНІХ НАФТОВИХ БІТУМІВ ТА ШЛЯХИ ЇЇ ВИРІШЕННЯ: ОГЛЯД

***Анотація.*** *Розглянуто основні закономірності процесу технологічного старіння нафтових бітумів, зокрема механізми та перетворення, що при цьому відбуваються. Наведено перелік основних лабораторних методів моделювання вказаних процесів, а також вказано, як змінювалась технічна суть методик від перших розробок і до сьогодні. Вказано ряд сполук, які можуть бути використані як інгібітори технологічного старіння, зокрема антиоксиданти та пластифікатори, а також ряд «натуральних» речовин, що здатні виявляти такі властивості.*

***Ключові слова:*** *модифікація бітуму, технологічне старіння, короткочасне старіння, гумат калію.*