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ORTO-PHOSPHORIC ACID AS AN ALTERNATIVE TO HYDROCHLORIC ACID – FOR CATIONIC BITUMEN ROAD EMULSIONS. REVIEW

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In this article the cationic bitumen emulsions are characterized – as popular binder for various road emulsions. There are considered the specific features of cationic bitumen road emulsions' formulations. There are presented the functions and specificities of the acids application in cationic bitumen road emulsions. The literary review is presented on potentialities of ortho-phosphoric acids application instead of the traditional hydrochloric acid. Chemical peculiarities of application are presented (as well as advantages and drawbacks of application) – for both the traditional hydrochloric acid and forward-looking ortho-phosphoric acid. As the advantages of ortho-phosphoric acid application for cationic bitumen road emulsions one can mention: simple replacement of acid in soap solution preparation, less corrosive acid, higher pH emulsions, acid is easier to store, fewer fumes, not regulated in some countries, unlike hydrochloric acid.

The potentialities are considered for application of ortho-phosphoric acid, as an effective component of cationic bitumen emulsion for application in various bitumen emulsion technologies, including the technologies for making protective slurry road pavements, among which the most wide-spread application was found by ortho-phosphoric acid in special fast-setting Slurry Surfacing systems, which possess a number of advantages over the same systems based on hydrochloric acid. The main of those advantages are as follows: such application eliminates the need for acid dopes in bitumen, provides a quick-traffic slurry system that works in cooler temperatures and at night, no need to change the usual latex or SBS grades, can use normal break retarders, mix controllable with cement in the field.

Key words: cationic bitumen road emulsions, hydrochloric acid, ortho-phosphoric acid, emulsifier.

Introduction

Bitumen road emulsions present the advanced material having currently the wide use both in the world and in Ukraine – for motor-roads construction and maintenance. It is possible to use road emulsions as a binder for plenty of road technologies. In spray applications the emulsion is used for surface dressing (chip seal), fog seal, scrub seal, graded aggregate seal, tack coat, prime coat, penetration macadam and dust control. In mix applications it is used for slurry seal, microsurfacing, cape seal, open-graded cold mix, dense-graded cold mix, soil stabilization, pre-coated chips, stockpile mix and recycling asphalt pavement (RAP) (Sidun, 2019).

Both by their formulations (application of either acid or alkali) and by pH-index, the emulsions are classified and divided into cationic and anionic. The cationic emulsions are more wide-spread, as far as they better interact with acidic aggregates (due to pulling and creation of insoluble amine-silicates), which

in their turn are most often used in road construction. Furthermore, the cationic emulsions, due to neutralization reaction and again creation of insoluble amine-silicates, interact also with the base (alkaline) aggregates. The anionic emulsions interact only with the base materials – due to pulling and creation of insoluble calcium soaps (Les emulsions de bitume, 2007).

Bitumen phase and water phase, as a rule, shall necessarily be a part of formulation for cationic bitumen road emulsion. In the role of bitumen phase there may be "pure" bitumen or bitumen with additives (polymers, adhesion promoters and solvents). Into the water phase there shall be included water, emulsifier and acid – as the main components. As secondary ones there may be stabilizers (calcium chloride or other soluble salts) and thickeners. SBR-polymer (latex) is also often added into the produced and cooled bitumen emulsion. Acids are the important component of cationic bitumen road emulsion, as far as they allow adjusting water phase pH (and pH of emulsion itself). Moreover, many cationic emulsifiers (diamines, imidazolines, amidoamines, to name three) are supplied in a water-insoluble neutral form and need to be neutralized with an acid like hydrochloric, phosphoric, acetic or sulfuric before the cationic form is generated. But there is also emulsifying agent of another type (fatty quaternary ammonium salts), which is used for production of cationic emulsions. Those are water-soluble salts as produced and do not require the addition of acid to make them water-soluble. They are stable, effective cationic (positively charged) emulsifiers. (Delmar R. Salomon, 2006)

As a rule, both in the world in general and in Ukraine in particular for cationic bitumen emulsion the hydrochloric acid is used, although such application may lead to a number of technological, economic and ecologic problems.

Objective of this article

The target is to present the review of potentialities for application of ortho-phosphoric acid for cationic bitumen emulsions – in replacement of the traditional hydrochloric acid.

Discussion

The emulsifiers used in cationic emulsions often need to be activated by acid addition to generate positive charge upon emulsifier molecule. Till present time the most widely-used acid has been the hydrochloric one. Still, in a number of countries there may be happening problems in hydrochloric acid supply. And this acid is also highly corrosive. The emulsifiers' producers offer the range of cationic emulsifiers, which can be used with alternative acids or (in some cases) even without the need of using any acid. Alternative acids may provide advantages in performance indicators upon the end-application of emulsion. Reaction of acid with aggregate (and obtained change of pH) make influence to a substantial degree upon the cationic emulsion breakage. Moreover, the acid choice makes influence upon the process, while the resulting products potentially will make influence upon the adhesion (Fig. 1) and rheology of the residue (AkzoNobel, 2012).

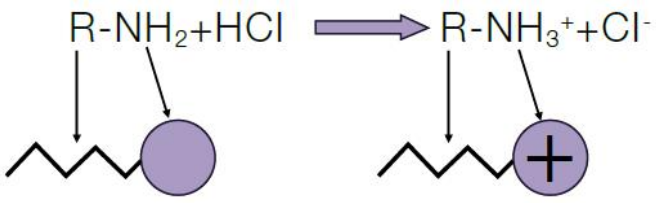

Fig. 1. Insoluble form / water-soluble cationic form (AkzoNobel, 2012).

In general, the application of acid in cationic bitumen emulsions can be characterized by the following theses: used to activate the N based emulsifier into cationic; dosage adjusted to achieve a certain pH (1 – 4.0); HCl is most common acid; some special formulations use phosphoric acid; concentration of the acid is not important (the set point is a given pH).

The emulsifiers for rapid-setting emulsions on the basis of “diamine” can be used with acetic acid, although this choice in the USA can be narrowed due to the requirements of normative documents. Water phase pH shall be adjusted till 3-4, while emulsifier dosage shall be increased by 10–20 % to provide for reactivity, comparable with that one of the hydrochloric acid. The application of ortho-phosphoric acid can improve the reactivity of limestone. (Fig. 2).

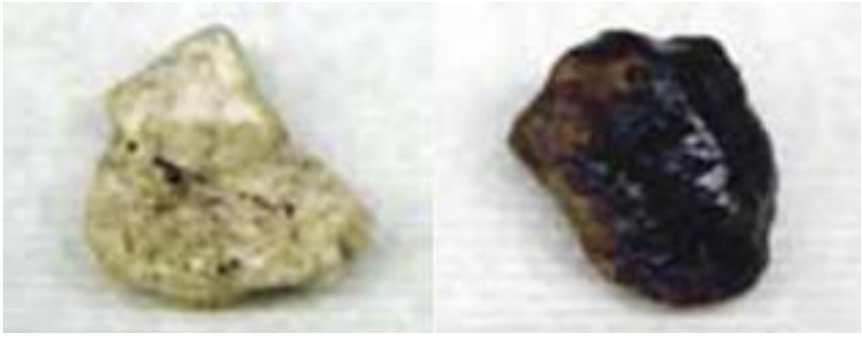

Fig. 2. Limestone after 1 hour soaking in bitumen emulsions and rinsed with water. Emulsion on hydrochloric acid (to the left) or emulsion on ortho-phosphoric acid (to the right) (AkzoNobel, 2012).

Ortho-phosphoric acid is also used for production of emulsions for Slurry Surfacing, providing for the high rate of cohesion strength build-up for the wide range of bitumens and forming blacker pavement (AkzoNobel, 2012; James, 2005, James, 2006). For Slurry Surfacing technology the optimum would be high acid bitumen, normally derived from a Venezuelan crude oil. In cases where this is not readily available (in case when low-acid oxidized bitumens from heavy oil or other ones are used) it can be difficult to produce emulsion formulations that perform well.

In general, Slurry Surfacing technology in the developing countries is not wide-spread due to a number of reasons: to reach the standard ratios it is necessary to use the expensive high acid import bitumen; during emulsion production they use rather aggressive hydrochloric acid (HCI), which can lead to equipment damage and requires obtaining license for dealing with precursors; when working with hydrochloric acid the higher labor safety level shall be guaranteed for the staff. Therefore, the usage of hydrochloric acid not only leads to the rise of technology cost, but also demands the entire chain of additional technological modifications both with regard to the working place for the staff and the production equipment both when it is installed and during its operation (Pyshyev, 2015; Sidun, 2020) .

By (AkzoNobel, 2013) there has been specially developed Redipave system to produce an emulsion for fast set - fast traffic Slurry Surfacing with low acid bitumen derived from paraffinic crude. However, Redipave works equally well with high acid binders. Furthermore, the ortho-phosphoric acid itself, same as water phase and Redipave emulsions, is less corrosive than products based on hydrochloric acid or other acids (Fig. 3). pH-value of the emulsions is higher, usually 3-4, in comparison with pH 1-3 for those ones produced by the traditional formulations. As a result, the corrosion is decreased both in the emulsion plant and in the paving equipment. Systems on ortho-phosphoric acid show exceptionally fast cohesion build-up, while it makes them especially suitable for work in cool weather and at a night time. The chemistry of this system differs, and some types of chips, which show unsatisfactory reaction in the system with hydrochloric acid, can give good performance with ortho-phosphoric acid. Moreover, the top-layers done with Redipave system look definitely blacker than those ones done with application of the traditional systems, while that results from the method of emulsion interaction with cement in Slurry Surfacing (lower level of soluble $CaCI_2$ reduces potential white staining on cured surface) (AkzoNobel, 2013).

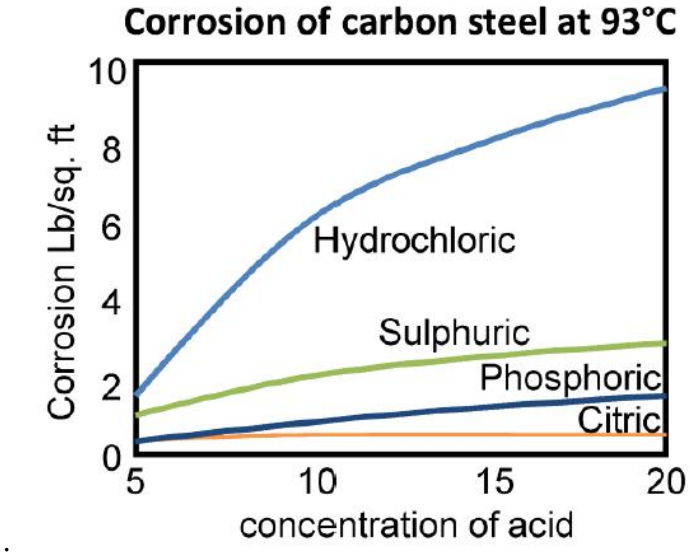

Fig. 3. Dependence of corrosion on concentration of some acids (Hogendoorn , 2016).

In (Hogendoorn, 2016) there are presented the main advantages of ortho-phosphoric acid for cationic emulsions: simple replacement of acid in soap solution preparation; less corrosive acid, higher pH emulsions; acid is easier to store, fewer fumes, not regulated in some countries, unlike hydrochloric, and disadvantages: complexity of storing and using two acids, restricted range of compatible emulsifiers. There are also shown the advantages for Slurry Surfacing: eliminates the need for acid dopes in bitumen, provides a quick-traffic slurry system that works in cooler temperatures and at night, no need to change the usual latex or SBS grades, can use normal break retarders, mix controllable with cement in the field, and disadvantages: not compatible with hydrated lime filler.

The investigations (Sidun, 2019) also assert the expediency of using ortho-phosphoric acid both for the cationic bitumen emulsions and Slurry Surfacing (Sidun, 2020).

In (Sidun, 2019) it is stated that the main difference in physical-technical indices of emulsions on hydrochloric and ortho-phosphoric acids consists in the lower values of breaking index and emulsion pH, while it means higher reactivity of this emulsion. The worse indices of stability during storage mean (in emulsions on ortho-phosphoric acid) the possibility of worse bitumen emulsification during the emulsion production, i.e.: there is possibility of rapid emulsification of bitumen droplets after milling by colloid mill, while due to this phenomenon the droplets are from the very beginning larger than in the systems on hydrochloric acid. Besides, in course of testing on miscibility with mixtures of grained composition and breaking index there was noticed the increased stickiness and darker coloring of mixes on ortho-phosphoric acid – in comparison with the systems on hydrochloric acid. In general, based on the testing done, it is possible to confirm the efficiency of using ortho-phosphoric acid for production of slow-setting cationic bitumen emulsions.

In (Sidun, 2020) there was proven the possibility and efficiency of slurry-surfacing systems application based on oxidized bitumens on ortho-phosphoric acid and Redicote C-320E emulsifier, with reaching the efficient indices of cohesion strength build-up rate and wet track abrasion for the pavement – in comparison with more wide-spread and known systems on hydrochloric acid. Besides, this system is less dependent upon the aggregate reactivity than hydrochloric-acid-based systems, while it provides for usage of actually all aggregates which correspond to the grading requirements for the Types of the mixes.

In its turn, in (Krutko, 2008) the study of adsorption interaction of alkylpropylenediamine and alkylpropylenepolyamine emulsifiers (produced by CECA, France) on liquid/gas and liquid/solid interfaces depending on nature of salt-forming acid counter-ion and pH of solution is carried out.

Interaction between the mineral materials of various nature and the components of bitumen emulsion is analyzed. It is just in this article, that the comparison is presented for the usage of exactly the hydrochloric acid and ortho-phosphoric acid for bitumen emulsions. The authors state that colloid-chemical characteristics of investigated cationic surfactants at the constant pH-value actually do not depend upon the nature of counter-ion of salt-forming acid in solution.

There also exist a number of patents popularizing the application of emulsion exactly with ortho-phosphoric acid. The invention (Jorda, 2016) relates to a bituminous emulsion comprising at least one bitumen, at least one emulsifier, phosphoric acid or a derivative thereof, at least one aqueous phase, and at least one particular additive. The invention also relates to a process for preparing said emulsion as well as the use of the emulsion to improve the resistance to stripping of a cold-cast mix.

In (Antonov, 1968) there is mentioned that in order to increase the water resistance and mechanical strength of the treated mineral mixtures, ortho-phosphoric acid is additionally introduced into the acid bitumen emulsion. Phosphoric acid activates the clay fraction of the soil. As a result of the interaction with iron and aluminosilicate particles, phosphate is synthesized to the ground, which significantly improves the water resistance and mechanical strength of the mixture.

Conclusions

1. A number of companies is already offering the emulsifiers for cationic bitumen emulsions, which interact successfully with ortho-phosphoric acid: amidoamines derivatives, polyamines, or mixed emulsifier, but their choice is rather restricted.

2. As it was shown by literary review, the bitumen emulsions based on usage of ortho-phosphoric acid have much more advantages than drawbacks. The restricting factor for the development of just such type of cationic bitumen emulsions is low degree of awareness on advantages of such emulsion and the restricted choice of emulsifiers for application with ortho-phosphoric acid.

3. Among the row of bitumen-emulsion road technologies the largest application of ortho-phosphoric acid was found in special fast-setting Slurry Surfacing systems, which have a number of advantages over the same systems on hydrochloric acid.

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ОРТОФОСФОРНА КИСЛОТА, ЯК АЛЬТЕРНАТИВА СОЛЯНІЙ ДЛЯ БІТУМНИХ ДОРОЖНІХ КАТІОННИХ ЕМУЛЬСІЙ. ОГЛЯД.

Охарактеризовано бітумні катіонні емульсії як популярне в'яжуче для різних дорожніх технологій. Розглянуто особливості складу бітумних дорожніх катіонних емульсій. Наведено функції та особливості застосування кислот у бітумних дорожніх катіонних емульсіях. Наведено літературний огляд можливості застосування ортофосфорної кислот для катіонних бітумних емульсій взамін традиційної соляної кислоти. Приведено хімічні особливості застосування, переваги та недоліки застосування традиційної соляної і перспективної ортофосфорної кислоти. Перевагами застосування ортофосфорної кислоти для бітумних дорожніх катіонних емульсій є: простота під час заміни кислоти в ємності для водної фази бітумної емульсії: кислота спричиняє меншу корозію поверхней, дає змогу виготовити бітумну емульсію з вищими значеннями водневого показника pH емульсії, простота зберігання, менша кількість парів, не потрібно ліцензії на роботу з прекурсором, на відміну від соляної.

Оглянуто можливість застосування ортофосфорної кислоти як дієвого компонента катіонної бітумної емульсії для застосування в різних бітумно-емульсійних технологіях, зокрема і технологіях для влаштування тонкошарових захисних покриттів автомобільних доріг. Серед них найпоширеніша ортофосфорна кислота у спеціальних швидкотвердних системах Сларрі Сурфейсінг (литі емульсійно-мінеральні суміші), які мають низку переваг порівняно з такими самими системами на соляній кислоті. Основними з цих переваг є: виключає необхідність використання висококислотного бітумного в'яжучого, виготовленого з важкої нафти, забезпечує швидке тверднення тонкошарового покриття з литої емульсійно-мінеральної суміші, дозволяє працювати за низчих температур, що дає змогу виконувати роботи і вночі, без проблем співпрацює із полімерними добавками та звичними регуляторами розпаду, дає можливість регулювати розпад суміші на місці за допомогою специфіки використання цементу.

Ключові слова: бітумні дорожні катіонні емульсії, соляна, ортофосфорна кислоти, емульгатор.