Development of new compositions for dust control in the mining and mineral transportation industry

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How to cite this article: Kondrashova N.K., Kireeva E.V., Zyryanova O.V. Development of new compositions for dust control in the mining and mineral transportation industry. Journal of Mining Institute. 2021. Vol. 248, p. 272-280. DOI: 10.31897/PMI.2021.2.11

Abstract. Dust control in summer and winter periods is a topical problem associated with conducting open pit mining operations; however, at negative temperatures the additional requirements are imposed on dust suppressants. Preventive compositions are proposed, in which light and heavy gas oils, obtained from catalytic cracking and delayed coking, are used as base components. Involvement of heavy fractions allows to increase the flash point, thereby reducing the flammability of dust suppressant, improve its adhesion properties by increasing the content of polyaromatic hydrocarbons and reduce the cost of the final product. In order to improve low-temperature and adsorption properties of developed dust suppressants, heavy oil residues (cracking residue and tar) are included in their composition in various concentrations: 2-10 wt.%. Alternative compositions of dust suppressants, obtained by water emulsification of vinylated alkyd oligomer, are developed; the ability of this dispersion to form strong films on dusty surfaces is examined. The efficiency of using aqueous solution of vinylated alkyd oligomer as a summer dust suppressant is demonstrated. The results of this study include the development of new preventive compositions with improved low-temperature properties and confirmation of the theoretical part of the study by the results of performance tests on a laboratory facility.

Key words: open pit mining; dust formation; dust suppressants; plant polymers; oil products; heavy oil residues

Introduction. This study is devoted to the issues of mining technology development and the safety of mining operations in the extreme conditions of negative temperatures, where the work has to meet high environmental standards. In Russia, the share of open pit mining – in particular, in ore deposits – amounts to about 70% of the total production. Development of the mining industry is accompanied by an increase in the excavation depth up to 400 m (in the future – 450-600 m), complications of quarry space ventilation and deterioration of working conditions in terms of gas and dust factors [7]. Some developments along with a new understanding of environmental problems and the deep mining strategy for cleaner mine production are presented in paper [14].

The coal industry of Russia is developing and increasing the rate of production, by 2030 it is planned to obtain 410 million tons of coal [9, 13]. The State Register of Mineral Reserves of the Neryungri and Syllakh deposits in the Far Eastern Federal District, the Republic of Sakha (Yakutia) showed that the republic accounts for 47% of explored coal reserves in the Eastern Siberia and the Far East [1], but not more than 7% have been developed or are under development now [11]. Coal production of the subsidiary of Tigers Realm Coal Limited in Russia (Beringovsky coal basin) increased by 131% over the year and reached 576 thousand tons [2].

Despite the demand for coal and its derivatives, there are unresolved problems associated with its handling. Extraction of more than 1,000 tons leads to a release of over 100 m³ of enrichment waste, which poses a threat to human health due to generation of technical dust. The largest share of harmful contaminant emissions is accounted for by drilling and blasting operations – about 35%, loading and transport operations – 40%; large amounts of dust accumulate in the quarry areas [3, 10].

Minute dust particles lead to significant atmosphere pollution of quarries and adjacent regions [10]. Dust poses a serious threat to the safety and health of workers engaged in open pit mining and underground tunneling, where highly environmentally sustainable compositions are recommended [14]. The main reasons leading to diseases are associated with the level of dust...
concentration and its dispersibility, the frequency of inhalation, as well as the content of free silicon dioxide and the presence of adsorbed gases (carbon and nitrogen oxides, aldehydes and others) on the dust surface [10].

Problem statement. The harsh climate of Russia (Kemerovo, Kuzbass) and low negative temperatures are natural for open pit mines, and solution to the problem of dust control at low temperatures is quite urgent. The paper proposes to reduce the pour point of the final preventive agent by introducing depressants, such as cracking residue and tar. The mechanism of pour point reduction is driven by the ability of resinous-asphaltene compounds to adsorb on solid surfaces of paraffin crystals that are involved in lowering the pour point [14]. Differential scanning calorimetry of paraffin crystal morphology demonstrates that paraffin crystals of the oil dispersed system are the main contributors to the depressor effect on the addition of any depressant: heavy oil residues or polymethyl methacrylate [14]. The study of mining industry in China and the works of Chinese and Japanese researchers [15-18, 21, 24] show that the problem of dust control is relevant for these countries too. In order to effectively increase the ability of water to suppress coal dust, when used in the coal mine of Erdos (China), a formulation of surface active agents (surfactants) was proposed and the mechanism of synergy between them was investigated [23]. Field tests showed that the efficiency of dust suppression with a solution, containing surfactants of the first and second types in the concentration of 0.025 wt.% each, was more than 87 %, which was significantly higher than the result of using water and effectively reduced the concentration of dust in the 2104 fully mechanized coal face of the coal mine in Erdos (China) [23]. This experiment confirms the feasibility of developing environmentally sustainable aqueous compositions based on plant polymers.

The purpose of this paper is to develop preventive agents (PAs) based on oil products with addition of heavy oil residues to improve low-temperature properties of PAs and their ability to suppress dust in winter, as well as to introduce plant polymers as an alternative raw material base for obtaining dust-suppressing compositions for summer [6]. Summer compositions based on aqueous dispersions are highly environmentally sustainable and effective; in paper [20], authors investigate water-based liquid lubricants, which can act as emulsifiers in the presence of even a small amount of oil. Research on the possibility of obtaining aqueous dispersions based on plant polymers for the development of preventive agents is quite promising.

Methodology. Comparative tests were carried out for preventive agents on water and organic (oil) basis. Organic-based PAs consisted of basic components, such as catalytically cracked light (CCLGO) and heavy (CCHGO) gas oils, as well as light (LCGO) and heavy (HCGO) coker gas oils and their mixtures in a 1:1 ratio [22]. Additives used to improve low-temperature PA properties included cracking residue (CR) and tar (T), which are characterized by good adhesion properties that affect performance characteristics of the final product [5]. The agent had to firmly adhere to the mineral (treated) surface in the form of a thin polymolecular film, preventing the separation of a dust particle from the treated area. Water-based PA was obtained by water emulsification of vinylated alkyd oligomer (VAO).

Test results of dust-suppressing compositions are presented in Table 1. All test methods are described in paper [22].

As seen from Table 1, judging by the main technological parameters, water-based PAs show better results compared to organic ones, primarily in terms of fire-prevention (flash point) and environmental characteristics (organic content). However, the use of VAO in the winter period is impossible, since its frost resistance is extremely low (pour point equals 0 °C).
A method for assessing resistance of the proposed preventive compositions. To assess the resistance of the proposed preventive compositions to wind erosion, a chamber was designed to simulate the actual process of dust formation in the quarry (Fig. 1). The chamber consisted of a container with a soil sample and a cyclone, simulating the wind. The cyclone was hermetically connected to the chamber with samples. The efficiency of dust suppression was assessed by measuring the mass of dust particles that the cyclone tore off from the surface, treated with different preventive compositions.

Samples of sand, coal and urtite were analyzed as dusty materials. Urtite was needed to test the ability of preventive compositions to eliminate dusting of fine materials.

A method for assessing dust-binding properties of the preventive agents. The study of dust-binding properties of the PAs was carried out by a method based on vibration mixing of dust with the PA and further assessment of its sieve composition, which imitates destruction of the road surface.

Sieve analysis was performed as follows: dust of a certain fraction (d = 0.15-0.08 mm) in the amount of 50 g was mixed with a dust-binding agent in the amount corresponding to the consumption rate of 1 dm³ per m² of the roadway. The dust was mixed with the PA over the course of 5 minutes. Then the sample was screened through a set of sieves with a mesh diameter of 1; 0.3; 0.2; 0.15; 0.08 mm [12]. Amount of the formed fraction greater than 1 mm (wt.%) was a measure of dust-binding properties of the PA [12].

Discussion. PAs have been developed on the basis of catalytically cracked gas oil fractions with boiling ranges of 200-340 and 320-470 °C and delayed coker gas oils with boiling ranges of 220-359 and 340-480 °C. Light and heavy gas oils were mixed in a 1:1 ratio, then cracking residue or tar heated to a temperature of 50-70 °C was added to this base mixture in the amount of 2 wt.%, after which the mixture was stirred until a homogeneous mass was obtained.

Physical and chemical properties of the developed PA compositions are presented in paper [22]. Preventive compositions with the addition of heavy oil residues, such as cracking residue and tar, in the concentration of 2-10 wt.%, meet the requirements of modern technical standards (TUs) for existing preventive compositions: TU 38.1011322, TU 38.1011142, TU 0258-001-48899100-2004, TU 0258-020-38519207-2012. Addition of heavy oil residue thickens the system in terms of such parameters as viscosity and density, but within values allowed by TUs, from 2.68 to 3.12 mm²/s [22]. An increase in viscosity helps to reduce consumption of the preventive agent during its application. The flash point with the addition of heavy fractions of delayed coker gas oils, catalytically cracked

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**Table 1**

| Parameter                              | VAO | CCLG0:CCHGO | LC0:HC0G0 |
|----------------------------------------|-----|-------------|-----------|
| Pour point, °C                         | 0   | –52         | –48       |
| Flash point, °C                        | –   | 100         | 80        |
| Engler viscosity according to the viscometer of type V3-246, °E | 10-20 | 13.5 | 12.5 |
| Organic content, %                     | 3-5 | 100         | 100       |

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**Fig. 1. An installation for measuring dust entrainment**

1 – an offtake with the flow of entrained particles; 2 – a collector of dust particles; 3 – a flow of entrained particles; 4 – a sphere, where the cyclone simulates wind entrainment; 5 – a container with the examined dusty material.
gas oils and heavy oil residues increases from 82 to 103 °C, which makes it possible to reduce flammability properties of the preventive agent. The pour point of the compositions decreases from −45 to −50 °C for mixtures based on catalytically cracked gas oils; for compositions based on delayed coking gas oils, the pour point decreases from −35 to −46 °C [22].

It has been established that the mechanism of heavy oil residues (HOR) acting as depressants in PA mixtures is combined with the mechanism of reducing surface tension (ST) at the liquid-solid interface; the indicators of ST and pour point (PP) depend on the concentration of active HOR components and the viscosity of oil dispersed systems (ODS), therefore it is necessary to compare all the dependence curves of ST and pour points on HOR concentration. Dependence curves of ST and PP on HOR concentration in CCLGO:CCHGO and LCGO:HCGO fractions, taken in a 1:1 ratio, at a temperature of −10 °C are presented in Fig. 2.

When heavy oil residues are introduced to the base fractions, due to some surface activity of resinous-asphaltenic substances (RAS) that they contain, adsorption layers are formed on the surface of growing crystals of solid paraffinic hydrocarbons. These adsorption layers inhibit the growth of crystals and prevent the formation of a correct crystal 3D-structure. As a result of contact interaction between RAS and crystals of solid hydrocarbons, the strength of coagulation structures decreases, and, consequently, so does the pour point of the mixture with a 5 wt.% HOR concentration (point B in Fig. 2, a).

The addition of cracking residue to the mixture of CCLGO:CCHGO at a concentration of 5 wt.% lowers the pour point by 18 °C, from −35 to −53 °C. In the same dispersion medium at a concentration of 5 wt.%, tar reduces the pour point by 11 °C (Fig. 2). For PA mixtures based on CCLGO:CCHGO, the optimal concentration of CR and T is 5 wt.%. PP depression depends on the content of solid paraffinic hydrocarbons in the oil fraction; catalytically cracked gas oils contain half the amount of solid paraffinic hydrocarbons compared to the mixtures based on LCGO:HCGO. When the maximum permissible concentration of cracking residue in the mixture is exceeded, coagulation bonds between supramolecular structures of the mixture of catalytically cracked gas oils with cracking residue are formed throughout the entire system. For a deeper study of surface properties of the developed PAs, their wetting ability was studied by measuring contact angle (CA) values on a metal plate (Fig. 3).

The contact angle decreases at HOR concentration from 2 to 10 wt.%. Further addition of HOR to the composition leads to the thickening of ODS, and CA value begins to increase. After analyzing the changes in surface tension and contact angle of laboratory PA samples as a function of ambient temperature, a study was performed on a dependence of adhesion work on HOR concentration in PA mixtures on the basis of both CCLGO:CCHGO and LCGO:HCGO at −10 °C; the results are presented in Fig. 4.

![Fig. 2. Dependence of surface tension and pour point on CR and T content for the mixtures of light and heavy catalytically cracked gas oils (a) and delayed coker gas oils (b) at −10 °C](image-url)

1 – CCLGO:CCHGO+CR; 2 – CCLGO:CCHGO+CR – PP; 3 – CCLGO:CCHGO+T – PP; 4 – CCLGO:CCHGO+T – PP; 5 – LCGO:HCGO+CR; 6 – LCGO:HCGO+CR – PP; 7 – LCGO:HCGO+T – PP; 8 – LCGO:HCGO+T – PP
When adding HOR (both tar and cracking residue) to the PA composition, adhesion work increases only after the introduction of HOR in the concentration above 10 wt.% due to enhancement of intermolecular interaction between HOR RAS and the metal surface. At a 5 wt.% concentration of CR and T, a decline in adhesion work is observed due to decreasing viscosity of the system and the depressor effect. Surface tension and CA change extremely (non-linearly), confirming the hypothesis of mutually competing adsorption processes at the liquid-solid interface and on the solid surface of solid paraffin crystals (only at negative temperatures). Tar in the field of the solvent, based on the mixtures of delayed coker gas oils, shows a sharp decrease in adhesion work, when it is added in the amount of 10 wt.%, but then an increase in adhesion work is observed, which is associated with hydrocarbon composition of delayed coker gas oils due to a high resin content (twice as high as in catalytically cracked gas oils). An increase in adhesion work is explained by the interaction of highly condensed LCGO:HCGO hydrocarbons with tar RAS; active thickening of ODS is observed. Obtained extreme dependences confirm that the compositions of CCLGO:CCHGO and LCGO:HCGO in a 1:1 ratio with a concentration of CR and tar from 2 to 10 wt.% have good wetting properties, but mixtures with a 5 wt.% concentration have better ones, which is confirmed by the given graph (Fig.3).

Lubricating properties of PAs were estimated by measuring the average value of wear scar diameter (WSD) of steel balls on a four-ball friction machine (FBFM) in accordance with GOST 9490-75.

The addition of CR at a concentration of up to 5 wt.% does not improve lubricating properties of the base mixtures of delayed coked gas oils. At the same time, an increase in WSD from 0.665 to 0.689 mm is observed. There is also an increase in the size of RAS macromolecules and a decrease in intermolecular interactions of liquid elements with each other and with the solid surface, which leads to a drop in the strength of the supramolecular structure, a decline of film thickness, and, hence, to deterioration of lubricating capacity [22]. High content of cracking residue in the mixture negatively affects other technical characteristics of the compositions; therefore optimal compositions are the ones with CR concentration of 2-10 wt.%. 
With the addition of tar at a concentration of up to 2 wt.%, WSD decreases from 0.807 to 0.762 mm, with an increase to 5 wt.% it rises again to 0.803 mm. With the addition of 2 wt.% CR, lubricating properties of base mixtures of catalytically cracked gas oils are improved, and WSD decreases from 0.807 to 0.685 mm due to the fact that CR RAS, which form a thin and uneven film on the surface of friction pairs (steel balls), interact with each other.

Based on this analysis, a conclusion can be drawn that the optimal compositions from the viewpoint of low-temperature, surface, adsorption, wetting and lubricating properties are mixtures containing CCLGO:CCHGO (1:1) with a CR and T concentration of 2-10 wt.% and LCGO:HCGO (1:1) with a CR and T concentration of 2-10 wt.%.

Alternative compositions of dust suppressants for the summer period were obtained by emulsifying vinylated alkyd oligomer in water. The resulting dispersion was studied for its ability to form strong films on dusty surfaces. VAO was obtained by post-vinylation in several stages: oil alcoholysis with a trihydric alcohol in the presence of a base (LiOH) was carried out, monoglyceride was esterified with a phthalic anhydride, and then post-vinylation was performed in the presence of ditertiary butyl peroxide, followed by polyesterification and VAO production. The process was carried out under laboratory conditions on a standard unit for alkyd synthesis, consisting of a three-necked flask, a stirrer, a refrigerator and a thermometer. The result of studying the content of 3D polymer in films, obtained from aqueous dispersions of VAO [4], showed (Fig.5) that in films, obtained from aqueous dispersions of VAO on sunflower oil, the share of 3D polymer was 45-50 %, the same as in the solvent-borne analogue [4]. In case of using soybean oil in VAO, the share of 3D molecules was 35-37 % [4, 8].

Using a scanning atomic-force microscope Ntegra Prima [4], authors examined the structure of VAO dispersion films on the mica surface [4]. Figure 6 demonstrates the images of the VAO film from different angles. The films are homogeneous, only small irregularities of 1-2 nm size are visible — those can be identified as compacted spheres of VAO molecule after film formation under the influence of van der Waals forces [4].

Fig.5. Polymer concentration in various alkyd dispersions
1 – alkyd varnish PF-060; 2 – VAO on organic solvents; 3 – aqueous dispersion of VAO (alkyd on sunflower oil); 4 – aqueous dispersion of VAO (alkyd on soybean oil); 5 – PVA; 6 – acrylic-styrene dispersion

Fig.6. Image of an irregular surface of the film, formed by a water-based preventive agent:

– at a scan angle of 45°, – top view
Studies confirmed that dust suppressants based on aqueous dispersions of VAO have a variety of advantages: increased hardness, accelerated drying time, the possibility of their application by pneumatic or airless spraying, the possibility of their production using standard equipment for the synthesis of alkyl oligomers, absence of organic solvents and environmental safety [4].

For a comparative assessment of wind erosion resistance of the proposed PAs, a chamber was designed to simulate the process of dust formation (see Fig.1). The efficiency of dust suppression was estimated by measuring the mass of dust particles, which the cyclone tore off from the surface treated with the PA. The preventive agent was applied over the dusting material with a spray gun at a rate of 0.5 l per 1 m². Samples of sand, coal and urtite were analyzed as dusty materials. Table 2 shows the test data of dust particle entrainment before and after PA treatment. The experiments were carried out for dust-suppressing compositions on the basis of oil and aqueous dispersion of VAO.

### Table 2

| PA | Sand | | Coal | | Urtrite |
|----|-----| |      |     |        |
|    | Before treatment, g | After treatment, g | Share of entrainment, % | Before treatment, g | After treatment, g | Share of entrainment, % | Before treatment, g | After treatment, g | Share of entrainment, % |
| VAO | 1.200 | 1.178.2 | 1.81 | 1.200 | 1.157.88 | 3.51 | 1.200 | 1.146.5 | 4.50 |
| HCGO:LCGO+CR (5 %) | 1.200 | 1.154.4 | 3.80 | 1.200 | 1.146 | 4.50 | 1.200 | 1.140.4 | 4.95 |
| HCGO:LCGO+T (5 %) | 1.200 | 1.155.4 | 3.71 | 1.200 | 1.147.8 | 4.35 | 1.200 | 1.142.8 | 4.76 |
| CCHGO:CCLGO+CR (5 %) | 1.200 | 1.154.4 | 3.80 | 1.200 | 1.146 | 4.50 | 1.200 | 1.140.6 | 4.95 |
| CCHGO:CCLGO +T(5 %) | 1.200 | 1.155.7 | 3.69 | 1.200 | 1.148.04 | 4.33 | 1.200 | 1.143.1 | 4.74 |

PA treatment reduces dust entrainment (Table 2) – for example, when sand was treated with a VAO-based preventive composition, the percentage of entrained dust particles amounted to 1.81 %, which was the best value obtained. The same material, treated with oil-based compositions, demonstrated dust entrainment values of 3.69-3.80 %, which is a positive result and allows to achieve effective dust control. Oil-based compositions are effective, and they perform particularly well on sand and coal. Aqueous dispersions work better on nano-dispersed dusty materials, such as urtite. This is easily explained by dispersion microstructure: its particles are so small that they can envelop the smallest dust particles. The results obtained do not contradict the data of studies by P. Wang et al. [19, 25]. Basing on experimental results, the efficiency of dust suppression by spraying was determined both by the wettability of coal dust and the absolute value of diameter difference between the droplets and ΔD50 dust particles. As the diameter of coal dust particles increased, the efficiency of dust suppression by spraying first improved and then declined. According to the experimental study of micro-properties, the amount of hydrophilic oxygen-containing functional groups gradually declined with a decrease of particle diameter. As the particle diameter decreased, specific surface area of coal dust gradually increased, and the average diameter of internal pores decreased. Dust wettability declined with a decrease of particle diameter, which is confirmed by the results presented in Table 2.

Comparison of the developed dust suppressants to the existing agents shows that the proposed oil composition for dust control is a competitive product and meets the requirements for physical, chemical and technological properties of PAs. The cost of the developed oil composition is 25 rub/l, which is comparable to the existing analogue – “Universin”, the cost of which is 28 rub/l. Market analysis of domestic and imported compositions, such as Dustclean (Russia), ArcticLine (Poland), Duster (Germany), ArenaKleen (USA), shows that their costs vary in the range of 250-755 rub/l, which is economically unfavorable for domestic industries focused on import substitution.

The results of market analysis of summer dust suppressants confirm economic efficiency of the developed VAO-based compositions, since their cost in a diluted form (solution concentration up to
10 wt.%) is only 4 rub/l, while the costs of analogues, such as DustControl LQD (Russia), dust suppressants of potassium salts (Russia), “ROSA” (Russia), DirtGlue (USA), vary in the range of 55-620 rub/l (kg).

**Conclusion.** To solve the problem of dust formation during extraction, processing and transportation of mineral resources, universal oil- and water-based preventive compositions were developed. Proposed compositions offer solution to the problems of increasing the efficiency of extraction and transportation of solid bulk materials by mining and transport equipment and improving the environmental situation by reducing dust formation in temporary quarries and on highways.

As a result of conducted studies of the main physical and chemical (viscous and low-temperature) properties of various composite PA compositions, the following conclusions were made:

1. PAs were developed based on a mixture of light and heavy gas oils of destructive processes – catalytic cracking and delayed coking – in a 1:1 ratio depending on HOR addition (cracking residue and tar) in an amount of 2-10 wt.%. The mechanism of depressor and thickening effect of oil residues mixed with gas oil fractions was confirmed. Prototypes that meet the existing technical PA standards – “Niogrin”, “Severin” and “Universin” were obtained and selected.

2. Results of studying the effect of ambient temperature and HOR concentration in oil mixtures on surface properties of various ODS compositions (surface tension, contact angle, adhesion work) confirmed an assumption about the unity of adsorption mechanism of cracking residue and tar RAS on solid crystals of paraffinic hydrocarbons in the dispersion medium (DM) and on metal surfaces, which explains an extreme decrease in ST, CA, adhesion work and PP. It was proved that RAS of cracking residue are more effective than RAS of tar, since addition of CR at an optimal concentration of 5 wt.% into a mixture based on LCGO:HCGO (1:1) reduces surface tension from 34 to 27 $\cdot 10^{-3}$ J/m$^2$, whereas addition of tar at the same concentration into the same mixture reduces surface tension from 34 to 30 $\cdot 10^{-3}$ J/m$^2$ at 20 $^\circ$C.

3. Tribological (lubricating) characteristics of the developed PAs were examined by means of measuring the wear scar diameter on the FBFM. In CCLGO:CCHGO (1:1) mixtures, addition of tar at a 2 wt.% concentration reduces WSD from 0.807 to 0.762 mm, whereas addition of 5 wt.% increases it to 0.803 mm. The optimal compositions from the viewpoint of low-temperature, surface, adsorption, wetting and lubricating properties are mixtures containing CCLGO:CCHGO(1:1) or LCGO:HCGO (1:1) with CR and T at a concentration from 2 to 10 wt.%. 

4. Environmentally-friendly summer dust suppressants were developed from alternative sources of raw materials based on aqueous dispersion of vinlylated alkyd oligomer.

5. Comparison of physical, chemical and performance properties of PAs on the basis of aqueous dispersion of VAO and oil was carried out. It is shown that PAs based on aqueous dispersion of VAO have superior fire-prevention and environmental properties. In addition, VAO compositions anchor finely dispersed surfaces almost two times better than organic PAs, but due to their high content of water and its freezing at low temperatures, they can only be used in summer or during warm periods in autumn and spring. Oil-based preventive agents are more effective for treatment of coals, coarse dusty materials and in winter periods due to their low pour point; therefore, developed compositions are not in competition with one another, since their areas of application are different.

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The authors declare no conflict of interests.

The paper was received on 11 December, 2020. The paper was accepted for publication on 29 March, 2021.