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CHEMICAL MODIFICATION OF BITUMEN FOR STABLE ROAD CONSTRUCTION

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ABSTRACT
Nitric acid has been found to be an effective additive for bitumen modification to enhance its performance and make it more appropriate for road construction purposes. This paper aims to provide an overview of the effects of nitric acid on bitumen properties, its application in road construction, and the benefits it offers. The paper explores the various methods of modifying bitumen with nitric acid, such as pre-treatment of bitumen, addition during mixing, and surface treatment of aggregates. The effects of nitric acid on the properties of bitumen, such as viscosity and stability, are discussed. Nitric acid improves the adhesion of the bitumen to the aggregates, enhancing the mixture of asphalt and aggregates, leading to improved stability and durability of the road surface. The paper also highlights the potential benefits of using nitric acid in road construction with bitumen. These benefits include improved resistance to moisture and temperature variations, reduced deformation under heavy loads, increased rutting resistance, and longevity of the bitumen pavement. The use of nitric acid with bitumen also facilitates the use of recycled bitumen products, which is more environmentally sustainable.
Key words: Bitumen, longevity, deformation, modification, aggregate

INTRODUCTION

Highways make is one of the basic elements of the economy of any nation. In the construction of flexible pavements, bitumen plays the role of binding the aggregate together by coating over the aggregate. It also helps to improve the strength of the road. Road surface with neat bitumen can cause bleeding in hot climate, may develop cracks in cold climate and possess fewer loads bearing capacity. A common method generally used to improve the quality of bitumen is by modifying the rheological properties of bitumen by blending with organic synthetic polymers like rubber and plastics. It is seen that with an increase of rubber crumbs ratio in the mixture, the stability of asphalt concrete increases at extreme temperatures. It also significantly increases the abrasion resistance of the coating. The addition of plastics into molten bitumen also improves the properties of bitumen. Researchers are also modifying the bitumen properties by adding nanostructures of high molecular polymer compounds like carbon nanotube (CNT) although CNT is very costly material. Bitumen is basically composed of large number of aliphatic as well as aromatic saturated and unsaturated hydrocarbons. The physical properties of bitumen like softening point, ductility, and penetration can be tuned by changing the structures in the molecular level. Since many unsaturated aliphatic and aromatic compounds are present in bitumen, addition of small quantity of inorganic acids like sulfuric acid, nitric acid or perchloric acid in hot molten bitumen facilitates polymerization reaction and by this chemical modification bitumen having higher softening point is obtained. The softening point of modified bitumen can be controlled by selection of suitable inorganic additive, its concentration and reaction temperature. Many researchers studied the effect of addition of different polymers (like rubber, plastic) and inorganic nanostructures (like CNT) with bitumen to achieve the suitable properties of bitumen required for road construction.

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CHARACTERISTICS OF BITUMEN FOR ROAD CONSTRUCTION

Bitumen is a commonly used material for road construction due to its unique characteristics. Here are some of the primary characteristics of bitumen that make it an ideal choice for road construction:

1. The viscoelastic nature: Bitumen has a unique viscoelastic nature, which means it can behave both as a viscous liquid and an elastic solid. This characteristic makes bitumen flexible and allows it to adapt to the movement of the underlying surface or the traffic load. It makes bitumen suitable for road pavements and waterproofing.
2. Adhesive properties: Bitumen has excellent adhesive properties, which can bond it with the aggregates used in road construction. The adhesive property ensures that the asphalt mix can withstand the load and resist rutting, cracking, and stripping.
3. Durability: Bitumen is a highly durable material that can resist deformation, abrasion, and weathering due to its unique viscoelastic properties. Bitumen roads can last for many years with minimal maintenance.
4. Water resistance: Bitumen is a waterproof material that resists the ingress of water into the pavement structure. It prevents water from penetrating into the pavement structure and causing damage to the underlying layers.
5. Low temperature sensitivity: Bitumen hardened at low temperatures and flexibility increased at high temperatures, which means it can withstand temperature variations and remain stable in different weather conditions.

These characteristics make bitumen an important material for road construction, resulting in a long-lasting and safe road network for people to use.

IMPORTANT CHEMICAL REACTIONS

Chemical modification of bitumen can be done using nitric acid. The reaction between nitric acid (HNO3) and bitumen results in the formation of oxidized bitumen or the formation of nitro-compounds in the bitumen. Here are some possible reactions that can occur when bitumen is modified chemically using nitric acid:

1. Nitration: When nitric acid reacts with bitumen, it leads to the formation of nitro-compounds in the bitumen. This reaction is typically carried out at elevated temperatures to ensure a complete reaction. The nitration of bitumen can improve its physical and chemical properties, such as increased stiffness, improved adhesion, and higher melting points.
2. Oxidation: Nitric acid is a powerful oxidizing agent and readily reacts with the hydrocarbon molecules present in bitumen. This reaction can lead to the formation of oxidized bitumen, which has a higher asphaltene content than the original bitumen. The oxidation process can also induce changes in the molecular structure of bitumen, leading to improved physical properties such as higher softening points and higher resistance to aging.
3. Cross-Linking: Cross-linking of the bitumen molecules can occur when nitric acid is used to modify bitumen. Cross-linking leads to a more elastic and durable bitumen matrix, making it more resistant to deformation and fatigue.

The chemical modification of bitumen using nitric acid is typically carried out in specific and controlled conditions to ensure that the desired properties are achieved. The modification process can significantly enhance the performance of bitumen in applications such as road construction, roofing, and waterproofing. However, it is important to note that nitric acid is highly corrosive, and the reaction should be carried out under strict safety protocols to avoid any accidents.

ENVIRONMENTAL ADVANTAGES OF CHEMICALLY MODIFIED BITUMEN

The use of chemically modified bitumen using inorganic acids offers several environmental advantages compared to traditional bitumen. Here are some of the environmental benefits of using chemically modified bitumen using inorganic acids:

1. Reduced Energy Consumption: The production of modified bitumen using inorganic acids requires less energy than the production of traditional bitumen. This is because the chemical modification

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process requires lower temperatures, which leads to reduced greenhouse gas emissions and lower energy consumption.
2. Reduced Carbon Footprint: The reduced energy consumption and lower production temperatures in the chemical modification process result in a lower carbon footprint. This helps to mitigate the effects of climate change.
3. Increased Longevity: The chemical modification process can increase the lifespan and durability of the bitumen. This means that fewer materials will be required over time, reducing the need for maintenance, repairs, and replacement, which results in fewer greenhouse gas emissions.
4. Better Resistance to Environmental Factors: Bitumen exposed to sunlight, oxygen, and other environmental factors can undergo aging and oxidation, causing it to lose its properties over time. The chemical modification process using inorganic acids can protect the bitumen from these factors, resulting in a longer lifespan and less pollution from discarded materials.
5. Recyclability: Modified bitumen using inorganic acids can be recycled and reused in other projects. Reusing waste materials reduces pollution caused by the disposal of waste materials.

MATERIALS AND METHODOLOGY

BITUMEN

Bitumen grade of S-40 was collected from construction site.

NITRIC ACID

Nitric acid at a concentration of 60% is used for the chemical modification of bitumen.

PHYSICAL TEST OF BITUMEN

Physical tests of bitumen are conducted to determine the quality and characteristics of the material. The following are some of the equipments used to measure physical properties of bitumen

1.Ductility Measuring Machine
2.Standard Penetrometer
3.Ring and Ball Apparatus

CHEMICAL MODIFICATION OF BITUMEN

Chemical modification of bitumen is a process where specific chemical compounds are added to bitumen to enhance its physical and chemical properties, such as adhesion, stability, durability, and temperature sensitivity.
Chemical modification refers to the process of altering the structure, properties, or function of a molecule or material through chemical reactions. The goal of chemical modification is to create new compounds with improved properties or to tailor existing materials for specific applications.
Chemical modification can be achieved through various methods, including:
1. Functionalization - Adding or replacing functional groups to change the chemical and physical properties.
2. Crosslinking - Creating covalent bonds between polymer chains to improve mechanical properties like tensile strength, elasticity, and durability.
3. Polymerization - Joining small molecules, called monomers, together to form a larger polymer chain, which can have unique properties compared to individual monomers.
4. Oxidation/Reduction - Altering the oxidation state of an element in the molecule to modify its reactivity and properties.
5. Substitution - Replacing one atom or group with another to change the chemical and physical properties.
Chemical modification can be applied to a wide range of materials, including polymers, metals, ceramics, and biological molecules. It has extensive applications in the fields of materials science, engineering, biotechnology, and pharmaceuticals.

WHY DO WE USE NITRIC ACID IN CHEMIICAL MODIFICATION

Modification of bitumen by using nitric acid is a process called Bitumen Oxidation. When bitumen is oxidized with the help of nitric acid, it undergoes a chemical reaction that changes its physical and chemical properties. Here are some of the possible effects of modifying bitumen by using nitric acid:

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1. Increased stiffness: The oxidation process increases the stiffness of the bitumen, which means it can resist deformation and rutting of the road surface efficiently.
2. Improved adhesion: The modified bitumen has enhanced adhesive properties that help it bond better with the aggregates used in road construction. This improves the overall stability of the road surface.
3. Water resistance: The oxidation process increases the water resistance of the bitumen, making it suitable for use in waterproofing and sealing applications.
4. Reduced temperature sensitivity: The modification of bitumen using nitric acid can reduce the temperature sensitivity of bitumen, making it more stable in varying weather conditions.
5. Enhanced durability: The modified bitumen has superior durability compared to unmodified bitumen. It can withstand traffic loads, resist damage from weather, chemicals, and UV radiation, and provide a long-lasting pavement structure.

CHARACTERIZATION OF CHEMICALLY MODIFIED BITUMEN

The characterization of chemically modified bitumen using inorganic acid is essential to determine the physical and chemical properties of the final product. Here are some of the common methods used for characterizing chemically modified bitumen using inorganic acid:
1. Softening Point: The softening point is the temperature at which the bitumen becomes soft enough to lose its properties. The softening point of chemically modified bitumen can be determined by ASTM D36.
2. Penetration: Penetration is the depth in millimeters that a standard needle penetrates vertically into the bitumen sample under standard conditions. The penetration value can be determined by ASTM D5.
3. Ductility: Ductility is the distance in centimeters that a standard briquette of bitumen will stretch before breaking under specific conditions. The ductility can be determined by ASTM D113.
Overall, the characterization of chemically modified bitumen using inorganic acid is crucial to determine if the final product meets the specifications and requirements for different applications, including road construction, roofing, waterproofing, and other civil engineering projects. The specific characterization method used depends on the properties and requirements of the final product.

RESULT AND DISCUSSION

DUCTILITY TEST

Ductility apparatus consists of a rectangular tank that is provided with a copper or steel liner sheet. It has a built in heater for use in winters. A pump to circulate water for maintaining uniform temperature. The machine has a clutch to select appropriate speed during testing. To prepare a specimen we need a briquette mold is made of brass material, it has a base plate, two clips and two sides. The clips have holes one for the fixed end and other for the moving end while placed in the machine during testing. We would require three numbers of such briquette molds. We also need a thermometer or a temperature indicator in order to measure the temperature of water in the ductility apparatus.
To prepare the sample, heat the bitumen to a temperature about 75 to 100°C above the approximate softening point . Prepare a mixture of equal parts of glycerin and dextrin. Apply the mixture to the surface of the plate and interior of the sides of the molds. This is done to prevent the sticking of bitumen to the surface. Now pour the heated bitumen into the mold. Fill all the molds and allow it to cool in air for about 30-40 minutes and then keep the assembly along with the sample in water bath maintained at 27°C for a period of about half an hour.
Remove the sides of the mold and secure the assembly in the machine. Check that the pointer should read 0 or alternatively the initial reading. Now switch on the machine and put it to appropriate gear such that it runs at a speed of 50mm per minute while one end is remained fixed and the other end is pulled apart. Observe the sample and note down the distance at which the bitumen thread of specimen breaks. Note down the value for all the three samples. The mean of three reading observed to the nearest whole number is the ductility value of the sample. If the specimen does not break up to a

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distance of 75 centimeters the machine may be stopped and the ductility value reported as >75 centimeters. The ductility of bitumen depends on its grade.

NORMAL BITUMEN

OVERALL DUCTILITY = 48.46 cm.

CHEMICALLY MODIFIED BITUMEN

I.100g of bitumen sample was added with 5ml of 60% nitric acid

OVERALL DUCTILITY = 66.13 cm

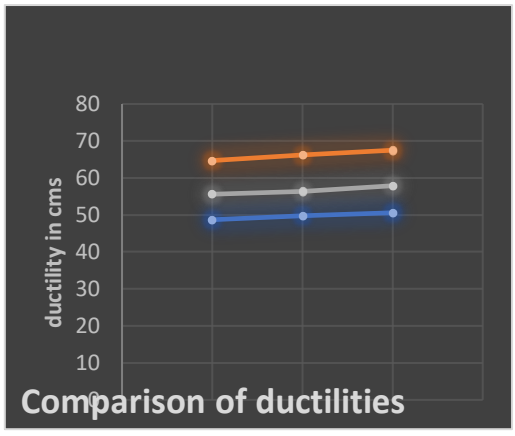
	1	2	3
(a)Initial reading cm	0	0	0
(b)Final reading cm	64.7	66.2	67.5
(c)Ductility=(b-a)cm	64.7	66.2	67.5

II.100g of bitumen was added with 3 ml of 60% nitric acid

OVERALL DUCTILITY =56.63 cm

	1	2	3
(a)Initial reading cm	0	0	0
(b)Final reading cm	46.9	48.7	49.8
(c)Ductility=(b-a) cm	46.9	48.7	49.8

	1	2	3
(a)Initial reading cm	0	0	0
(b)Final reading cm	55.6	57.9	56.4
(c)Ductility=(b-a)cm	55.6	57.9	56.4



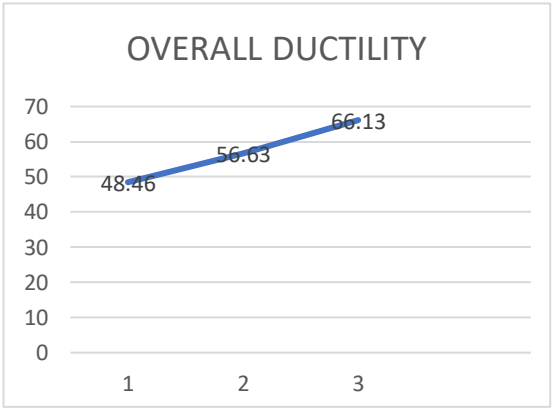


Fig (a) Bitumen sample in a brass mold

Fig(b) Placing the mold in a ductility

Fig(c) Measuring the ductility of the bitumen

Testing machine

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GRAPHICAL REPRESENTATION OF DUCTILITY VALUES OF BITUMEN AND CHEMICALLY MODIFIED BITUMEN

PENETRATION TEST:

The grading of Bitumen is done on the basis of its consistency. The consistency is determined by measuring penetration of bitumen. Penetration of bitumen is the distance travelled by a standard needle of a specific size, weight and shape under specified condition of time and temperature in one tenth of the millimeter. Penetration test is done by using standard penetrometer. A standard penetrometer comprised of a metal base, a weight and a carrier. The total rate of the carrier assembly including that of the penetration needle is 100 grams. It has a release knob as we push the knob the assembly is released and as we take out the pressure it is locked again. At the top, it consist of a dial which is graduated in one tenth of millimeter. Specimen is taken in a container having diameter of 55mm and a height of 35mm. 100 gram of load is attached on the top of the penetrometer needle. The penetrometer enables the load to be released exactly for 5 seconds.

The prepared specimen is allowed to cool it in atmospheric condition for one hour and then allow it to cool in water bath for one to one and half hour. Having placed a bitumen sample in water bath for one and half hour ensure that the whole of the sample is uniformly maintained at a temperature of 25°C. Bring the specimen at the base of the penetrometer. Take a penetration needle and clean it with benzene. Dry the needle and fix it in the bottom of the penetrometer. The needle assembly should have free movement and if required we can slightly lubricate. Now place the sample below the needle and bring the needle in contact with the top surface of sample. We allow the needle assembly to penetrate for 5 seconds. Note down the final reading after the 5 seconds when the needle is

	1	2	3
(a)Initial reading cm	0	0	0
(b)Final reading cm	19.3	17.6	18.4
(c)peneration=(b-a) cm	19.3	17.6	18.4

	1	2	3
(a)Initial reading cm	0	0	0
(b)Final reading cm	8.4	9.2	9.6
(c)peneration=(b-a)cm	8.4	9.2	9.6

automatically get locked. Repeat the same procedure for three times at the different location of the bitumen sample. The average of these three readings is taken as the penetration value of the bituminous sample.

NORMAL BITUMEN

OVERALL DUCTILITY = 18.43cm

CHEMICALLY MODIFIED BITUMEN

I.100g of bitumen sample was added with 5ml of 60% nitric acid

OVERALL DUCTILITY = 9.066cm

II.100g of bitumen was added with 3 ml of 60% nitric acid

	1	2	3
(a)Initial reading cm	0	0	0
(b)Final reading cm	12..4	13.8	14.5
(c)penetration =(b-a)cm	12.4	13.8	14.5

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OVERALL DUCTILITY = 13.566cm

Fig (e) Sample bitumen for penetration test

Fig (d) Placing the sample in the standard penetrometer

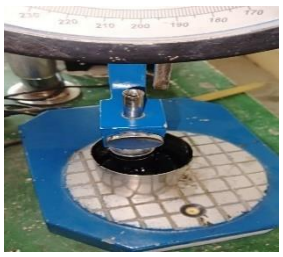
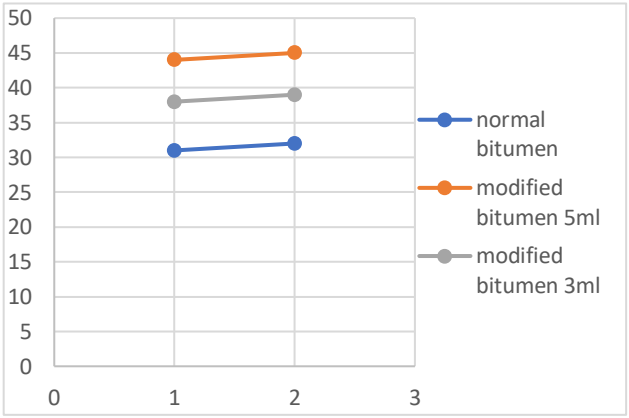
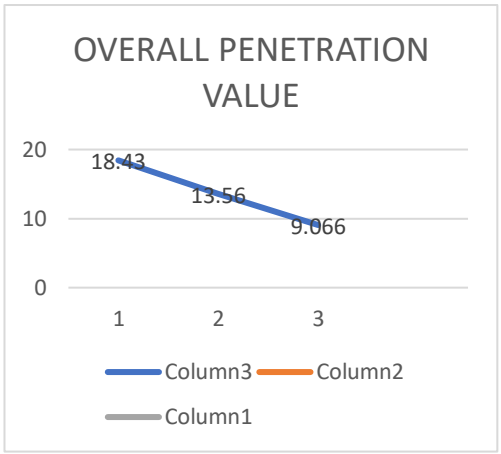


Fig (f) Testing of sample in standard





penetrometer.

GRAPHICAL REPRESENTATION

SOFTENING POINT TEST

The softening point of bitumen is the temperature at which the bitumen becomes soft enough to flow under a specified load or pressure. The softening point test is an important laboratory test for assessing the quality and suitability of bitumen for use in road construction. The following is the step-by-step procedure for the softening point test of bitumen:

The ring and ball apparatus comprises of a metal frame having three plates. The top plate have a hole for insertion of thermometer. The middle plate has two slots for placing the rings and the bottom one is a flat. The distance between the bottom of the ring placed and the top surface of the bottom plate is 25 millimeters. The cylindrical ring is tapered one and the diameter at top is 17.5 mm and its height is 6.4 mm. The centering guide has three pins such that they form an imaginary circle of diameter slightly larger than 7.5 mm to enable the movement of steel ball. The steel ball has diameter of 7.5 mm and its weight is 3.5 gram. The centering guide and ring fit each other and can be placed on the metal frame. A thermometer of range 120°C and the accuracy not less than 0.5°C is used. A hot plate connected through a energy regulator which is provided to regulate the rate of heating and a stirrer which is meant to maintain a uniform temperature in the bath.

Bitumen is heated to a temperature between 75 to 100°C above its softening point simultaneously take a glass plate and prepare a mixture of glycerol and dextrin. Apply the mixture on the surface, this is done to avoid sticking of bitumen to the plate. When the bitumen has acquired desired consistency pour the molten bitumen carefully in the rings. Allow it to cool for 30 minutes in air if required the excess bitumen can be removed using a hot sharp edged knife. Fill the beaker with a distilled water at a temperature of 5°C and the beaker is filled to such a level that the surface is about 50 mm above the level of specimen. Now assemble the ring and ball guide and place it on the metallic

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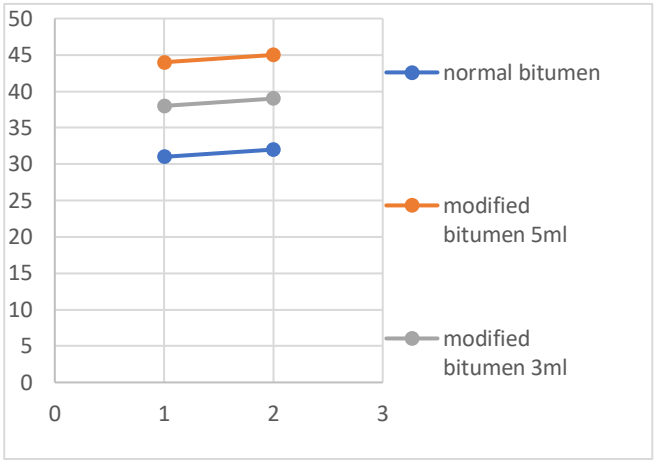

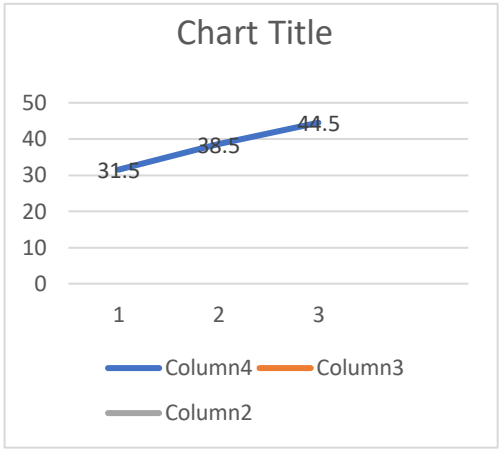

	1	2
(a)initial reading	0	0
(b)final reading	38	39
(c)softening point=(b-a) ℃	38	39

frame. Place the frame in water and leave for 15 minutes. After 15 minutes we take the steel ball which have been previously cooled at a temperature of 5℃ and place them on the top of ball guide.

	1	2
(a)initial reading	0	0
(b)final reading	31	32
(c)softening point=(b-a) ℃	31	32

Now place the assembly on the heating plate, fix the stirrer.

Switch on the hot plate and insert the thermometer. The heating should be done such a way the rate of increase of temperature is 5℃ per minute. Now we can control the rate using energy regulator. Now as the temperature rises the bitumen will become softened and the steel ball under its own weight will start falling down. Note down the temperature at which the ball touches the bottom plate.

NORMAL BITUMEN

OVERALL SOFTENING POINT = 31.5℃

CHEMICALLY MODIFIED BITUMEN

I. 100gm of Bitumen sample was added with 5ml of 60% of nitric acid

OVERALL SOFTENING POINT = 44.5℃

II. 100gm of Bitumen sample was added with 3ml of 60% of nitric acid

	1	2
(a)initial reading	0	0
(b)final reading	44	45
(c)softening point=(b-a) ℃	44	45

OVERALL SOFTENING POINT = 38.5

GRAPHICAL REPRESENTATION

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CONCLUSION

➢ Inorganic chemical additives can enhance the performance of bitumen-based materials and improve the quality, durability, and safety of road constructions.
➢ Improved Adhesion: Inorganic acids can improve the adhesion and cohesion properties of bitumen, increasing its bond strength to the road aggregates.

➢ Increased Durability: Inorganic additives like nitric acid can improve the durability of bitumen by reducing its oxidative aging, which can lead to cracking and deformation in asphalt pavements.

➢ Enhanced Stability: It can enhance the stability and strength of the road structure by improving the load-bearing capacity, reducing deformation, and preventing rutting and cracking.

➢ Better Resistance: They can improve the road's ice melting capacity, thereby reducing the formation of ice dams and potholes.

➢ Environmentally Friendly: Inorganic chemical additives are non-toxic and non-hazardous, which makes them eco-friendly and safe for the environment.

➢ Overall, the use of inorganic chemicals with bitumen can significantly improve the performance and durability of road construction materials, reduce maintenance costs, and enhance the safety and comfort of road users.

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