

# Novel Bitumen Chemical Rejuvenation by Using Dodecenyl Succinic Anhydride (DDSA)

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**Abstract:** Most of roads are formed of a mixture of mineral aggregates and bitumen that acts as a binder to form a solid pavement. Unfortunately, roads deteriorate over time due to accumulated damage from vehicles and also to weathering conditions and therefore must be repaired to continue to provide their safety function.

In this sense, recycling or reuse of pavement material is an environmental and cost effective way for road maintenance. However, the main concern of this technology is the ageing process that undergoes the bituminous phase in the road so that cannot be used as a direct substitute for virgin binder. This contribution presents results of a laboratory study on the use of a novel chemical rejuvenator (dodecenyl succinic anhydride, DDSA) able to soften hard bitumen with the purpose of restore the properties of aged binders.

The results obtained point out that the addition of small amounts of DDSA remarkably reduce binder consistency in a wide range of temperatures, since viscosity and storage modulus are clearly shift to lower values. This effect is quantitatively more marked than that of typical physical rejuvenators.

This outcome is attributed to the existence of chemical reactions between DDSA and bitumen polar compounds giving rise to new molecules with attached alkenyl chains. Changes observed in the FTIR spectra and the presence of new ester groups, confirms the reaction of DDSA with hydroxyl groups in polar bitumen molecules.

**Keywords:** road rejuvenation, bitumen, asphalt, rheology.

## 1. Introduction

Bitumen (asphalt in America), is the residue from crude oil distillation, and is a complex material basically composed of hydrocarbons along with some other molecules which contain small percentages of heteroatoms (sulphur, nitrogen and oxygen). Bitumen compounds can be broadly classified by chromatographic techniques into four different fractions (usually referred to as SARAs): saturates (S), aromatics (A) and resins (R), which make up the maltenes, and asphaltenes (As). The complexity, aromaticity, heteroatom content, and molecular weight increase in the order  $S < A < R < As$  [1]. A colloidal model, consisting of asphaltenes being dispersed into an oily matrix of maltenes and peptized by resins, is traditionally used to describe bitumen behaviour [2,3].

Because of its properties, bitumen is considered the most suitable material to be employed as a binder for paving [4]. Despite its small proportion (about 5 wt.%), bitumen constitutes the continuous phase in a pavement, and is its only deformable component. Consequently, it mainly controls the performance of a road [5]. Unfortunately, even the best designed and constructed road pavements deteriorate over time under the combined effects of traffic loading and weathering. The most common distresses are rutting, or permanent deformation at high temperatures [6], and thermal cracking, or thermal fracture due to lack of flexibility at low temperatures [7].

Consequently, due to bitumen ageing or deterioration asphaltic pavements require frequent maintenance and repairing operations that usually consist in replacing the upper layer. These operations employ a considerable proportion of raw materials (mineral aggregates and bitumen) and consume large amounts of energy. Thus, recycling asphaltic pavements creates a cycle of reusing materials that optimizes the use of natural resources. The use of reclaimed asphalt pavement is a useful alternative from both an ecological and an economical standpoint because it represents an alternative for energy and cost saving in asphalt pavements. However, as a consequence of the bitumen aging during pavements' service, the recycling processes usually use the so called rejuvenating agents which provide a practical means for restoring the mechanical properties of the aged binders

reducing the needed additional virgin binder. In general, rejuvenating agents can be broadly classified in two groups: real rejuvenators and softening additives. The main difference between them is that a rejuvenating agent will restore the chemical structure of aged binder, while a softening agent reduces the overall viscosity of the binder. Both of them are generally composed of petroleum products containing polar and aromatic oils, waste vegetal or engine oils, and other additives. [8-9]

Here, a novel chemical rejuvenator (dodecyl succinic anhydride, DDSA) is evaluated. The main goal is to analyse the rejuvenating capacity of the selected agent in terms of chemical reactions with bitumen compounds.

## 2. Materials and methods

### 2.1. Materials

Two bitumens with a penetration grade of 13/22 and 85/100 were used as base material for the modification and supplied by Repsol SA. (2-Dodecyl-1-yl)succinic anhydride was used for bitumen modification and was supplied by Sigma-Aldrich. This alkenyl succinic anhydride consists of a tetrapropenyl moiety, a mono unsaturated branched hydrocarbon, and a succinic anhydride group. Engine oil was also employed as a reference material.

### 2.2. Methods

Blends of bitumen and additives were prepared by mechanical stirring in an open low-shear batch mixer (80 mm diameter) using an agitator IKA RW-20 (Germany) equipped with a four-blade propeller (50 mm diameter). Additives were slowly added at the initial stages of the mixing process. Samples were processed for 1 hour, at 150°C and a rotational speed of 1200 rpm. After mixing, the resulting binder was poured into a small can and then stored in a freezer at -25°C to retain the obtained morphology. Additive concentration was fixed to 3 wt.%.

Flow measurements, at 60°C were performed in a controlled-strain Rheometrics Ares Rheometer (Germany) using a plate-and-plate geometry (25 and 50 mm diameters).

Dynamic measurements were used for the linear viscoelastic characterization of all three materials including the base bitumen. Tests were performed in strain-control rheometer ARES 33, Rheometric Scientific at -30°C. Samples were tested on torsion bar geometry with the dimensions of 55-12-2.7 mm.

## 3. Results and discussion

Rejuvenating agents are designed to restore the original characteristics to aged bitumen binders in order to soften the aged binder and create a broad-spectrum rejuvenation that replenishes the volatiles and dispersing oils while promoting adhesion. Typically, bitumen regenerators are comprised of 40-90% low viscosity components and also may include plasticizers, anti-aging agents and other additives that could improve the performance of the resulting binders [10]. From a rheological point of view the softening degree may be assessed by means of flow curves at a specific temperature.

Figure 1-2 show the effect of DDSA and oil on the viscous behaviour at 60°C for two bitumens of different penetration. All samples present a Newtonian behaviour in the whole shear rate range.

The flow curves of modified bitumens, presented in Figure 1-2, point out that, regardless the base bitumen, the addition of both DDSA and engine oil yields changes in sample rheology since, a steep drop in Newtonian viscosity is clearly noticed. This effect is more pronounced in the case of DDSA. This result is very important because the efficiency of the rejuvenator is normally evaluated in terms of viscosity.

Taking into account that aged bitumens would present higher viscosity and would be stiffer than fresh bitumen, the obtained results point out the potential use of DDSA as a bitumen rejuvenator, being more effective than the reference motor oil.

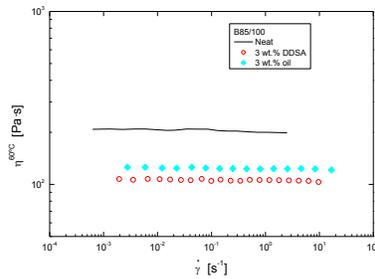


Fig. 1: Flow curves, at 60°C, for neat bitumen 85/100 and bitumen modified with DDSA and oil.

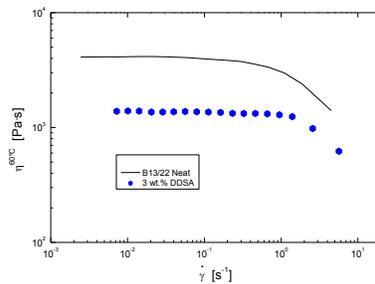


Fig. 2: Flow curves, at 60°C, for neat bitumen 13/22 and bitumen modified with DDSA.

The rheological behaviour of a modified bitumen should also be studied in the low in-service temperature region. Thus, oscillatory shear measurements within the linear viscoelasticity region, at  $-30^{\circ}\text{C}$ , were carried out on the systems studied above (Figures 3-4). Figure 3 shows the evolution with frequency of the elastic modulus ( $G'$ ), obtained from oscillatory torsion experiments. As can be observed, the storage modulus presents values around the glassy modulus (approximately  $10^9$  Pa) especially at high frequencies. In addition, as correspond to the glassy region all the samples display, at the studied temperature, a predominantly elastic behaviour ( $\tan\delta < 1$ , Figure 4).

It is important to underline that the glassy state leads to a brittle behaviour which facilitates the development of thermal cracking. Therefore, binder becomes fragile to light impacts due to traffic loads and causes crack initiation and propagation and eventually leads to the deterioration of the pavement. Thus, an ideal modifier should be able to shift the glassy behaviour towards lower temperatures. Thus, in the low temperature region ( $-30^{\circ}\text{C}$ , Figure 3), DDSA and engine oil addition give rise to a decrease of  $G'$ . This fact can be interpreted as a reduction in binder stiffness in this region. In practice, the elastic modulus at low temperatures is an important factor for the strain tolerance and fatigue resistance of a binder, directly related to the fracture behaviour of asphalt mixes. Too high binder modulus at low temperatures makes the asphalt sensitive to thermal and load induced cracking. Another important result may be also deduced from Figure 4 where both additives lead to a notable increase of the loss tangent at  $-30^{\circ}\text{C}$  exhibiting an enhanced rheological response at low temperatures. Taking into account that loss tangent is the ratio of the energy dissipated to that stored per cycle of deformation, an increase in this parameter yields positive effects on the performance of a road asphalt binder, because this softer structure presents higher ability to relax the internal stresses originating from traffic load. Consequently, the absorbed energy due to traffic loads is more easily dissipated, pointing out a higher flexibility, at low temperatures, and so better resistance to thermal cracking.

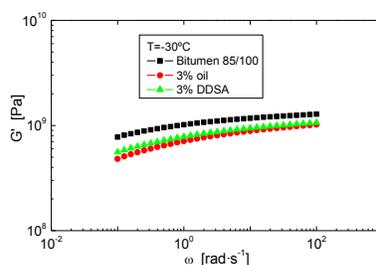


Fig. 3: Frequency dependence of the storage modulus, at  $-30^{\circ}\text{C}$ , for neat bitumen 85/100 and bitumen modified with DDSA and engine oil.

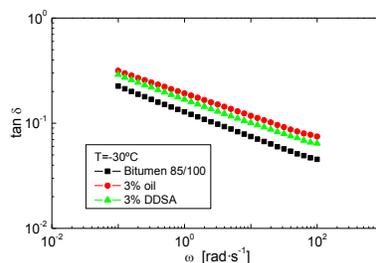


Fig. 4: Frequency dependence of the loss tangent, at  $-30^{\circ}\text{C}$ , for neat bitumen 85/100 and bitumen modified with DDSA and engine oil.

The mechanism of modification of the rheological response is different. In the case of non-reacting systems the decrease in viscosity and elastic modulus is mainly due to the plasticizing effect provoked by the addition of a liquid with low viscosity. Thus, the molecules of the engine oil would merely act as a diluent of heavier bitumen structures leading to a modification of the colloidal stability.

However, in the case of DDSA, even though physical effects may also be partially responsible of the modification of the mechanical behaviour, chemical interactions could explain the higher rejuvenation capacity. Thus bitumen presents a considerable amount of polar molecules with the presence of hydroxyl groups which can be esterified with anhydrides. An example of the reaction schemes for esterification (succinylation) is shown in Figure 5, where the most polar fraction of bitumen (asphaltenes) is considered. The introduction of anhydride group into the bitumen molecular alters the size and polarity of the resulting molecule since a long alkyl chain is attached the structure.

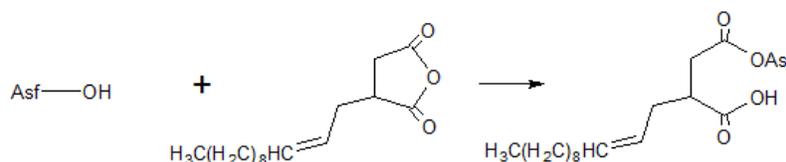


Fig. 5: Chemical reaction involving bitumen polar compounds (asphaltenes) with DDSA.

The proof of anhydrides modification of bitumen molecules is indicated by the FTIR spectra (Figure 6). Figure 6 shows the spectra of unmodified and modified bitumen and pristine DDSA. There is no apparent peak of an ester bond in the native bitumen or DDSA. However, after bitumen modification with DSSA, the peaks of ester carbonyl bond appeared centred at  $1710\text{ cm}^{-1}$ . Therefore, it might be concluded that esterification reaction occurred between bitumen and DDSA.

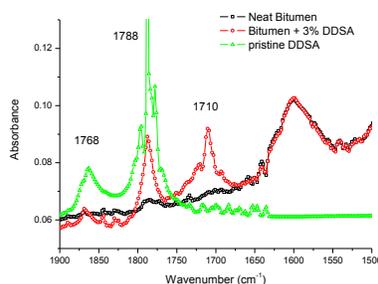


Fig. 6: Infrared spectra (FTIR) for bitumen neat bitumen 85/100 and bitumen modified with 3 wt% DDSA and pristine DDSA.

## 4. Conclusions

Both engine oil and DDSA can be potentially used as a rejuvenator in recycled bituminous pavement. Lower viscosity, at high in-service temperatures, and higher flexibility at low temperatures are pointed out after the addition of rejuvenators. The rejuvenation capacity of DDSA is higher especially at high in-service temperatures. This fact is explained on the basis of chemical reactions between DDSA and polar bitumen compounds.

## 5. Acknowledgements

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