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"THE USE OF FATTY AMINE DERIVATIVES TO SLOW DOWN THE AGE-HARDENING PROCESS IN BITUMEN"

A.D. James and D. Stewart
Akzo Chemicals Limited, Hollingworth Road,
Littleborough, Lancashire, OLl5 OBA, U.K.

ABSTRACT

This paper contains a brief summary of the mechanism of bitumen ageing and a review of the application of anti-oxidants in bitumen technology. The utilisation of fatty amine derivatives to slow down the age-hardening process is presented.

INTRODUCTION

Because bitumen is an organic material it is inherently prone to reactions such as evaporation and oxidation and finally breakdown.[1] These processes are referred to as the ageing of bitumen. The result of ageing is an increase in binder viscosity, a stiffening of asphalt mixes, and a reduction in pavement flexibility$_1$ which can lead to the formation and propagation of cracks within a road and its ultimate failure.

Although bitumen ageing may be inevitable, several specific actions can be taken to retard its onset and propagation.

MECHANISM OF AGEING

The ageing of bitumen can be considered to begin as soon as it leaves the refinery, but the rate of ageing is very dependent on its origin and method of processing.
Petersen[2] has listed three fundamental composition related factors that govern possible age-hardening of bitumens: -

i) Loss of oily components of bitumen by volatility or absorption by porous aggregates.

ii) Changes in the chemical composition of bitumen molecules from reaction with atmospheric oxygen.

iii) Molecular structuring that produces thixotropic effects, i.e. steric hardening.

Significant hardening of the binder can occur in hot-mix production, storage, transport and laying. 3 This is primarily due to the loss of volatiles and surface oxidation.[4] This initial phenomenon can be ameliorated by a greater control of hot mix production temperatures[5], and the use of inert blanket gases. Initial bitumen ageing could also be reduced by the replacement of hot mix by cold (emulsion) mix processes.
Ageing continues once the mix has been laid and oxidation is dependent on the depth within a road.[6] Oxidation is at its highest in the surface layer and decreases rapidly through a dense mix. Mix designs which allow the penetration of air have been shown to accelerate ageing.[7] Bitumen film thickness influences the ageing process and a rigorous approach to mix design could eliminate a significant portion of the bitumen ageing problem.[8]

Petersen[2] found that Ketones and sulfoxides were the major oxidation products formed during oxidative ageing, but anhydrides and carboxylic acids were formed in smaller amounts. The photochemical action of light is. important in determining the rate of surface oxidation.[9]

The oxidation of bitumen involves the formation of asphaltenes from resins[10]$_1$ and Kasahara et a1[11] found that a decrease in bitumen penetration due to oxidation, corresponded to an increase in the asphaltene content of the bitumen.

BITUMEN ANTI-OXIDANTS

Traxler[1] made the distinction between anti-oxidants and dispersants, (Table 1). A dispersant was considered to function by resolublising precipitated asphaltenes formed by oxidative reactions. An anti-oxidant in contrast chemically reacts with a bitumen and arrests oxidative polymerisation, which is propagated by the reaction of free radicals with oxygen or peroxides.

TABLE 1
Bitumen Anti-Oxidants and Dispersants, (Traxier)

Substance Used		Function
1.	Amino-mercapto benzothiazole; phosphorus sulfides	Metal (iron) anticatalyst
2.	Para-isopropoxy diphenyl -amine; thio diphenylamine(Phenothiazine)	Antistaining (antirusting) compound, for photosensitive asphalts
3.	Long-chain fatty acids	Antistaining (antirusting) compound, for photosensitive asphalts
4.	Selenium and tellurium oxides, dioxides	Prevention of hardening
5.	Pour depressor	Prevention of hardening of waxy asphalts
6.	Alkylated catechol; naphthyl-amines; copper naphthenate	Antirust ("staining") compound
7.	Pine tar	Antioxidant for oily and resin components; dispersant

Martin[12] conducted an extensive laboratory evaluation of anti-oxidants for bitumen. Although no highly efficient systems were found, Zinc diethyldithiocarbamate, a peroxide decomposer, was found to be effective in the dark, whereas N phenyl N isopropyl p phenylene-diamine, a free radical trap, was effective against photo-oxidation.

Consequently, the Australian Road Research Board have conducted field trials using Lead diamylthiocarbamate as an anti-oxidant,[13] and have found a significant reduction in the rate of bitumen hardening. The mechanism of oxidation is considered to be thermal rather than photo-oxidation.

This concurs with the studies carried out by van Gooswilligen et al,[4] who postulated that because the application of hot mix is carried out at temperatures less than 200C, that bitumen oxidation is predominantly a non-free radical reaction. Thus conventional anti-oxidants, which work by mechanism of free radical scavengers are ineffective in reducing bitumen oxidation.
Hydrated lime has been found to reduce bitumen oxidative hardening.[14] A synergistic mechanism has been suggested, where lime reduces the formation of oxidation products by the removal of oxidation catalysts and promoters, and also the removal of reactive polar molecules, which otherwise would react with the oxidation products and form asphaltenes.

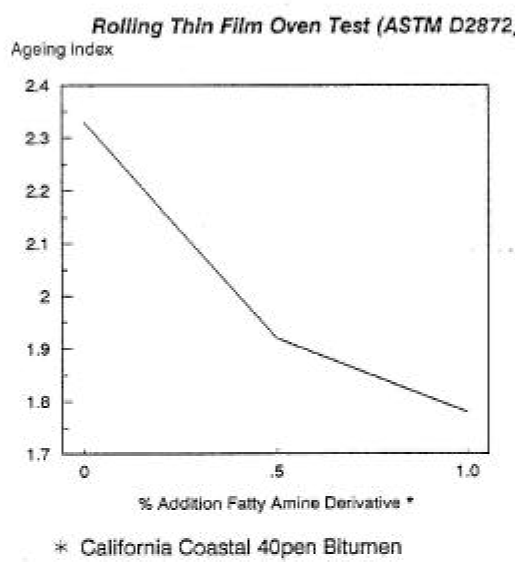
FATTY AMINE DERIVATIVES AS ANTI-OXIDANTS

Fatty amine derivatives have long been known for their ability to delay the onset of bitumen oxidation.[15]

a) Rolling Thin-Film Oven Test, (RTFO)

The susceptibility of binders to ageing can be determined in accelerated tests, where thin films of bitumen are exposed to an oxidising atmosphere, 75 mins at l63~C). In the RTFO the "ageing index" is the ratio of bitumen viscosity after the test to that of the untested sample. The presence of low levels of a fatty amine derivative, (1KG to 1000KG of bitumen), significantly decreases the "ageing index", (Figure I).

FIGURE 1



A glc method has been developed which can detect free residual fatty amine derivatives in hot binders. 17 Table II lists the RTFO data for a Venezuelan 70 pen binder containing 1.0% of a fatty amine derivative, (2 hours at l40C prior to the RTFO). The results indicate that the amine acts as a dispersant, before and after the test. The fatty amine derivative disperses flocculated asphaltenes before the test, shown by a decrease in the bitumen penetration and viscosity as compared to the standard binder. After oxidation, although it seems that the fatty amine derivative has been oxidised it still is highly effective in dispersing the oxidation products, (asphaltene formation). The undetected fatty amine derivative is still functioning as a dispersant, and not allowing the colloidal balance of the bitumen to be altered by the formation of flocculated asphaltene micelles.

TABLE II

RTFO Data for 70 pen Venezuelan Bitumen

Sample	Before RTFO			After RTFO		
	pen	viscosity,(cp)	% amine	pen	viscosity,(cp)	% amine
70 pen bitumen	70	350	-	46	400	-
70 pen + 1% FAD	78	250	0.9	54	350	0.3

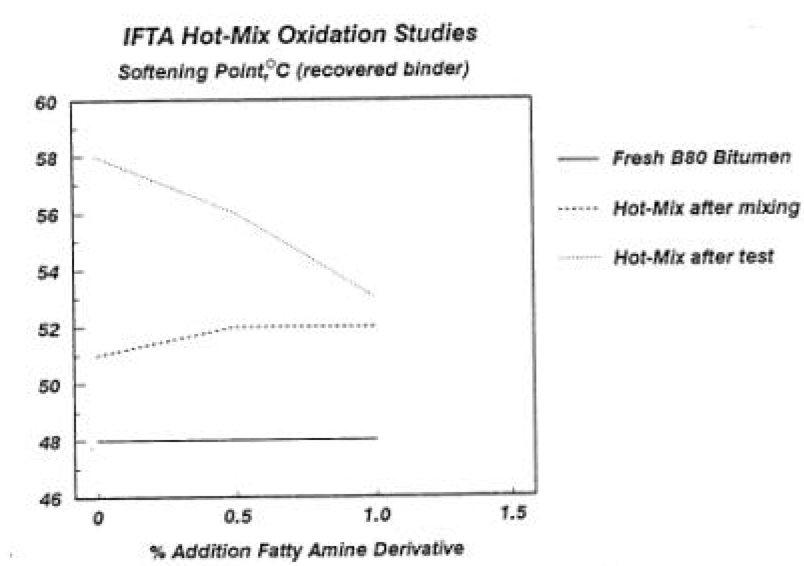
b) Initial Hot Mix Oxidation

Considering that the initial oxidation of a hot mix is one of the most important factors that determine its final performance, the Ingenieurgesellschaft fur Technische Analytik, (IFTA) have developed a method to monitor this phenomenon. [17]

The IFTA method consists of preparing a bed of hot-mix, (l80C) through which is passed air or nitrogen, (500 mi/mm), for 60 minutes. The softening point, (ring and ball) of the binder is measured before and after the test. This method allows the effect of the loss of volatiles and hardening due to oxidation to be separated.

The addition of a fatty amine derivative practically eliminated the hardening of the bitumen film by oxidation, although the loss of volatiles is, of course, not affected, (Figure II).
Again the fatty amine derivative is considered to act as a dispersant.

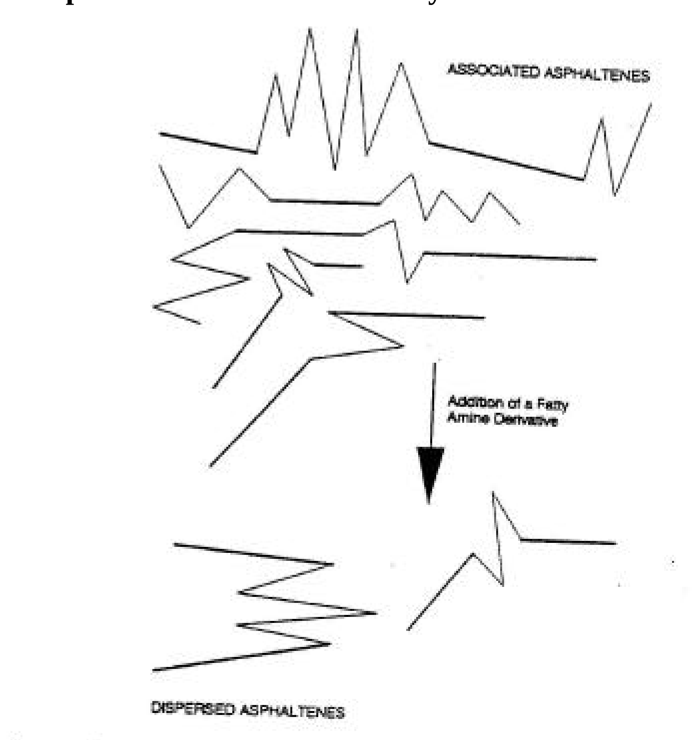
FIGURE II



c) Dispersant Mechanism

Mechanistically, a fatty amine derivative is considered to peptise and solvate single asphaltene molecules, and therefore reduce the size of individual asphaltene aggregations, (Figure III).

FIGURE III
Dispersant Mechanism of a Fatty Amine Derivative.



This dispersion phenomenon can be shown by measuring the flocculation ratio of a bitumen. The flocculation ratio is a measure of the asphaltene aggregation within a bitumen. A high flocculation ratio indicates a very aggregated bitumen. Figure IV illustrates the solvation effect of a fatty amine derivative, on a polymer modified and oxidised bitumen[1] by a reduction in the flocculation ratio after the addition of the fatty amine.

CONCLUSIONS

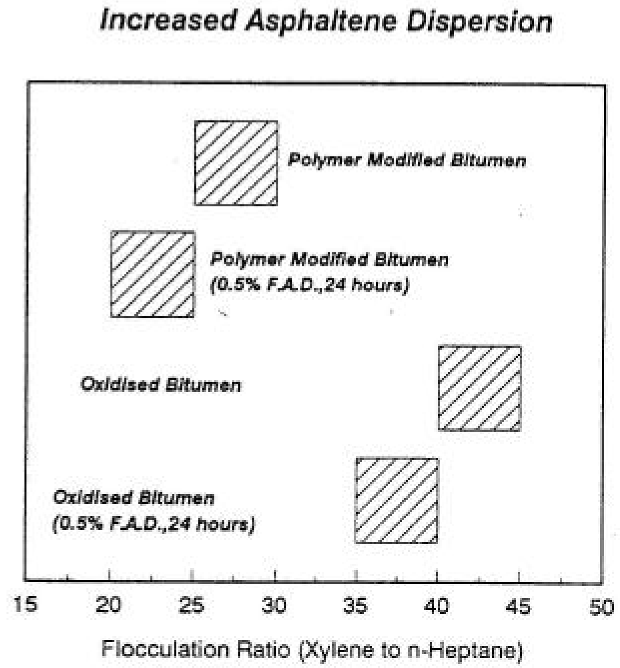
a) Therefore conventional anti-oxidants have been found to be ineffective when used in bitumen.

b) Fatty amine derivatives have been found to be highly efficient dispersant agents in oxidised bitumens, ie maintain the colloidal balance of a bitumen after oxidation.

c) The fatty amine derivative is thought to deter the formation of flocculated asphaltene micelles.

d) This phenomenon is only considered to be significant in the initial stages of hot-mix production and compaction.

FIGURE IV
Solvation Effect of a Fatty Amine Derivative



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