

Patented Nov. 18, 1952

2,618,558

## UNITED STATES PATENT OFFICE

2,618,558

PHOTOGRAPHIC DEVELOPERS COMPRISING  
AN N,N - DIALKYL-p-PHENYLENEDIAMINE  
AND A BENZENE SULFONATEPaul W. Vittum and George W. Kerridge, Roch-  
ester, N. Y., assignors to Eastman Kodak Com-  
pany, Rochester, N. Y., a corporation of New  
JerseyNo Drawing. Application April 12, 1949,  
Serial No. 87,118

8 Claims. (Cl. 95-88)

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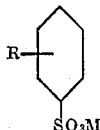
This invention relates to photographic de-  
velopers and particularly to photographic de-  
velopers having increased solubility.

It is known that photographic developers of the  
primary aromatic amino type are valuable com-  
pounds for producing fine grain black and white  
photographic images and also that these com-  
pounds, especially when they contain alkyl sub-  
stituents on one of the nitrogen atoms, are use-  
ful as developers in the production of colored  
photographic images.

One disadvantage of the primary aromatic  
amino developing agents, particularly the N,N-  
dialkyl-substituted p-phenylene diamines is that  
they possess rather limited solubility in the  
aqueous alkaline developing solutions. Because  
of their limited solubility, only limited amounts  
of the developing agents can be incorporated in  
the developing solutions and for this reason, the  
developing power of the solution is lower than  
it would be if a greater amount of developing  
agent could be used.

It is, therefore, an object of the present in-  
vention to provide an improved photographic de-  
veloping solution. A further object of the pres-  
ent invention is to provide a means for increas-  
ing the solubility of primary aromatic amino de-  
velopers, particularly N,N-dialkyl-substituted p-  
phenylene diamine developers. A still further ob-  
ject is to provide photographic color developing  
solutions in which increased quantities of de-  
veloping agents can be incorporated.

These objects are accomplished by incorporat-  
ing in the developing solution containing the pri-  
mary aromatic amino developing agent, a benzene  
sulfonate of the following formula:



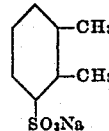
in which R represents hydrogen, an alkyl radical  
containing not more than five carbon atoms, that  
is, a methyl, ethyl, propyl, butyl or amyl radical,  
or a fused-on saturated carbocyclic ring, and M  
represents ammonium or an alkali metal radical,  
for example, sodium, potassium, or lithium.

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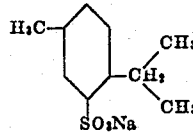
The following compounds may be employed ac-  
cording to our invention:



Sodium benzene sulfonate



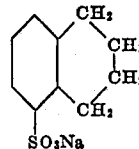
Sodium xylene sulfonate (o, m, or p)



Sodium p-cymene sulfonate



Sodium p-tert. butyl benzene sulfonate



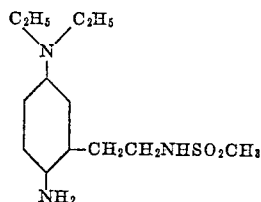
Sodium tetrahydronaphthalene sulfonate

When added to the developing solution in con-  
centrations varying from 20 to 200 grams per liter  
of solution, preferably from 50 to 100 grams per  
liter of solution, we have found that these com-  
pounds greatly increase the solubility of the de-  
veloping agent and therefore permit the addi-  
tion of maximum concentrations of developing  
agent to the developing solution. We prefer to  
use the sodium benzene sulfonates having one or  
more alkyl substituents of not more than five  
carbon atoms on the benzene ring. With these

agents we have obtained particularly good results with developing agents of the N,N-dialkyl-substituted p-phenylene diamines which are commonly employed as color developer in conjunction with a coupling compound which couples with the oxidation product of the developing agent.

Our solubility-increasing agents are especially useful with developing agents including N,N-dimethyl-p-phenylene diamine, N,N-diethyl-p-phenylene diamine, 2-amino-5-diethylamino toluene, the developing agents of Weissberger U. S. Patent 2,193,015 and the developing agents of Weissberger, Glass and Vittum U. S. patent applications Serial Nos. 731,420, 13,525 and 13,526, now Patents No. 2,548,574, No. 2,592,363 and No. 2,592,364, respectively.

An example of the effectiveness of the solubilizing agents of our invention as shown by the behaviour of a developer having the following structure:



4-amino-N,N-diethyl-m-(β-methylsulfonamidoethyl)-aniline

This developing agent is soluble to the extent of about 2 grams per liter in developing solutions of pH about 11. The solubility of the developing agent is increased to five grams per liter by the addition of 100 grams per liter of solution of sodium p-xylene sulfonate and to 10 grams per liter by the addition of 200 grams per liter of sodium p-xylene sulfonate. The resulting more concentrated developer solutions obtained by the addition of the sodium xylene sulfonate showed a marked increase in developing activity over the basic solution containing two grams per liter of the developing agent.

The following example illustrates a color developing solution which may be used according to our invention.

#### A.

3-methyl-4-amino-N-ethyl - N - (β-methyl-sulfonamido) ethyl aniline

Sodium sulfite .....	grams..	5
Sodium carbonate .....	do....	0.5
Potassium bromide .....	gram..	1
Sodium p-cymene sulfonate .....	grams..	100
Water to 1 liter.		

#### B.

Coupler (2,4-dichlor-a-naphthol) .....	grams..	2
Sodium hydroxide (10% solution) .....	cc....	10

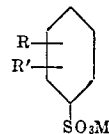
For use, B is added to A.

When used for the formation of color photographic images the developers of our invention may be used with any well-known coupler compounds such as those described in Fisher U. S. Patent 1,102,028, granted June 30, 1914, Mannes and Godowsky U. S. Patent 2,108,602, granted February 15, 1938, or Mannes, Godowsky and Peterson U. S. Patents 2,115,394, granted April 26, 1938 and 2,126,337, granted August 9, 1938.

It will be understood that the examples included herein are illustrative only and that our invention is to be taken as limited only by the scope of the appended claims.

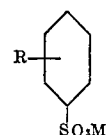
We claim:

1. A photographic developing solution comprising an N,N-dialkyl-p-phenylenediamine developing agent and a substantial amount of a compound of the following structure:



where R and R' are selected from the class consisting of hydrogen, alkyl radicals containing not more than five carbon atoms, and groups wherein R and R' together represent the atoms necessary to complete a fused-on saturated carbocyclic ring, and M is selected from the class consisting of alkali metal and ammonium.

2. A photographic developing solution comprising an N,N-dialkyl-p-phenylenediamine developing agent and a substantial amount of a compound of the following structure:



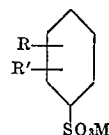
where R is an alkyl radical containing not more than 5 carbon atoms, and M is an alkali metal.

3. A photographic developing solution comprising an N,N-dialkyl-p-phenylenediamine developing agent and from 20 to 200 grams per liter of developing solution of a sodium benzene sulfonate having an alkyl substituent of not more than 5 carbon atoms on the benzene ring.

4. A photographic developing solution comprising an N,N-dialkyl-p-phenylenediamine developing agent and approximately 100 grams per liter of developing solution of a sodium benzene sulfonate having an alkyl substituent of not more than 5 carbon atoms on the benzene ring.

5. A color photographic developer in which the developing agent has increased solubility, comprising an N,N-dialkyl-p-phenylenediamine developing agent, a compound capable of coupling with the oxidation product of said developing agent, and a sodium benzene sulfonate having at least one alkyl substituent of not more than 5 carbon atoms on the benzene ring.

6. The method of increasing the solubility of N,N - dialkyl - p - phenylenediamine developing agents in photographic developing solutions, which comprises adding to the developing solution containing said developing agent, a substantial amount of a compound of the following structure:

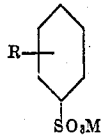


where R and R' are selected from the class consisting of hydrogen, alkyl radicals containing not more than five carbon atoms, and groups wherein R and R' together represent the atoms necessary to complete a fused-on saturated carbocyclic ring, and M is selected from the class consisting of alkali metal and ammonium.

7. The method of increasing the solubility of N,N - dialkyl - p - phenylenediamine developing agents in photographic developing solutions, which comprises adding to the developing solu-

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tion containing said developing agent, a substantial amount of a compound of the following structure:



where R is an alkyl radical containing not more than 5 carbon atoms, and M is an alkali metal.

8. The method of increasing the solubility of N,N - dialkyl - p - phenylenediamine developing agents in photographic developing solutions, which comprises adding to the developing solution containing said developing agent, from 20 to 200 grams per liter of developing solution of a sodium benzene sulfonate having an alkyl substituent of not more than 5 carbon atoms on the benzene ring.

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